Enantioselective Total Synthesis of (+)-Psiguadial B

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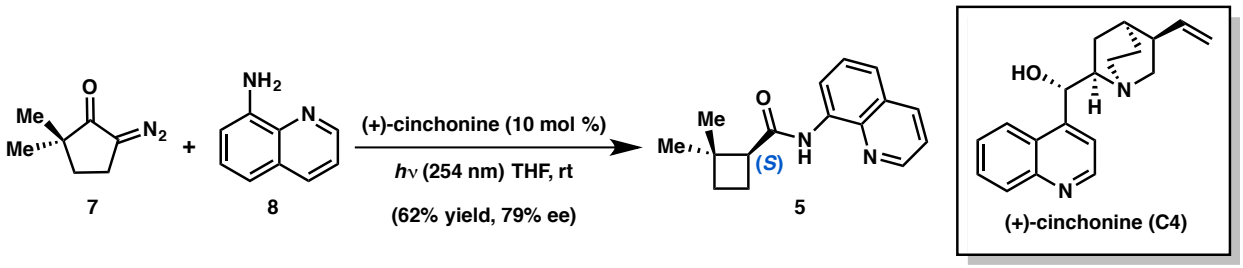
Supporting Information 1 (Experimental Procedures)

General Procedures. Unless otherwise stated, reactions were performed under a nitrogen atmosphere using freshly dried solvents. Tetrahydrofuran (THF), methylene chloride (DCM), acetonitrile (MeCN), *tert*-butyl methyl ether (TBME), benzene (PhH), and toluene (PhMe) were dried by passing through activated alumina columns. Triethylamine (Et_3N), N,N-diisopropylethylamine (DIPEA), and methanol (MeOH) was distilled over calcium hydride prior to use. Unless otherwise stated, chemicals and reagents were used as received. All reactions were monitored by thin-layer chromatography using EMD/Merck silica gel 60 F254 pre-coated plates (0.25 mm) and were visualized by UV, *p*-anisaldehyde, or 2,4-dinitrophenylhydrazine staining. Flash column chromatography was performed either as described by Still et al.[1] using silica gel (particle size 0.032-0.063) purchased from Silicycle or using pre-packaged RediSep®Rf columns on a CombiFlash Rf system (Teledyne ISCO Inc.). Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD with Prodigy cryoprobe (at 400 MHz and 101 MHz respectively), a Varian 400 MR (at 400 MHz and 101 MHz, respectively), a Varian Inova 500 (at 500 MHz and 126 MHz, respectively), or a Varian Inova 600 (at 600 MHz and 150 MHz, respectively), and are reported relative to internal $CHCl_3$ (^{1}H, δ = 7.26), and $CDCl_3$ (^{13}C, δ = 77.1) or C_6H_5 (^{1}H, δ = 7.16), and C_6D_6 (^{13}C, δ = 128). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), or mixed (MM) ionization mode, or obtained from the Caltech Mass Spectral Facility in fast-atom bombardment mode (FAB). Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system with a Chiralcel AD-H column (4.6 mm x 25 cm).

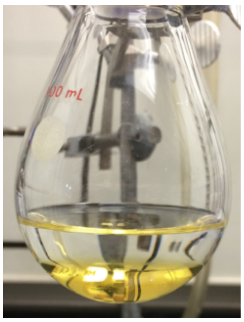
Large-scale preparation of enantioenriched cyclobutane 5.

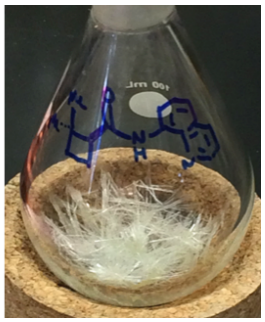


To a flame-dried, 1 L quartz flask was added 8-aminoquinoline (**8**) (12.9 g, 89.5 mmol, 3.00 equiv) and (+)-cinchonine (**C4**) (879 mg, 2.99 mmol, 0.100 equiv). The flask was evacuated and backfilled with N_2 three times and dry THF (600 mL) was then added via cannula. Diazoketone **7**[2] (4.12 g, 29.8 mmol, 1.00 equiv) was added last via syringe and the reaction was irradiated with stirring using a Honeywell 254 nm lamp at room temperature. Reaction progress was monitored by TLC (72-168 hours are typically required for complete conversion on this scale, and rotation of the flask every day provided faster conversion).[3] Upon completion, the reaction mixture was concentrated *in vacuo*, the solids (**C4**) were taken up in DCM, and the suspension filtered. The filter cake was washed with DCM three times and the filtrate was concentrated *in vacuo* to give a crude residue that was purified by silica gel flash chromatography (isocratic: 6% EtOAc/hexane) to provide **5** (4.69 g, 62%) as a pale-yellow solid. The enantiomeric excess was determined to be 79% by chiral SFC analysis (AD-H, 2.5 mL/min, 20% IPA in CO_2, λ = 254 nm): t_R (major) = 4.23 min, t_R (minor) = 5.64 min. $[\alpha]_D^{25.0}$ = –66.0° (c = 0.560, $CHCl_3$).

Recrystallization procedure:

Enantioenriched cyclobutane **5** was dissolved in a minimal amount of DCM in a 100 mL round-bottom flask. An equal amount of hexanes was carefully layered on top of the DCM to form a biphasic mixture. The layers were allowed to diffuse overnight to provide **5** as white needles. The supernatant was concentrated under reduced pressure and this process was repeated again to provide additional **5** (3.50 g total, 83% recovery of theoretical total of the desired enantiomer, 46% overall from **7**): $[\alpha]_D^{25.0}$ = –109° (c = 0.720, $CHCl_3$).





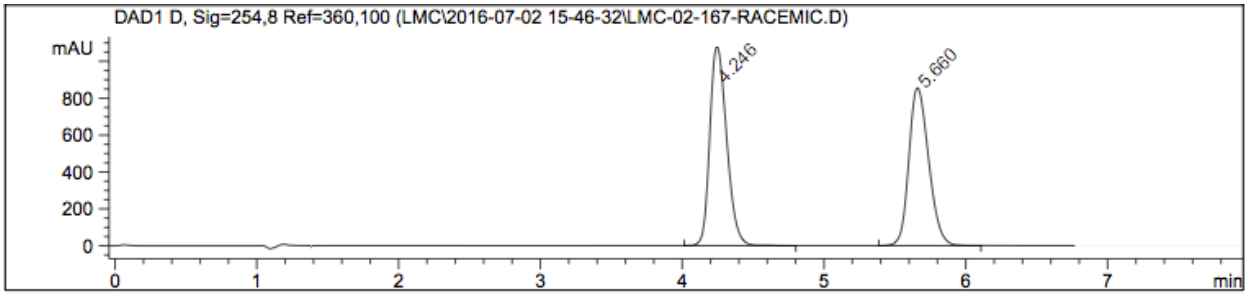
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.80 (t, *J* = 1.8 Hz, 1H), 8.79 (dd, *J* = 13.6, 1.6 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.52 (q, *J* = 8.2, 7.5 Hz, 1H), 7.48 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.07 (ddd, *J* = 9.1, 8.2, 0.9 Hz, 1H), 2.48 (dq, *J* = 11.4, 9.4 Hz, 1H), 2.06 (dtd, *J* = 11.6, 8.6, 3.3 Hz, 1H), 1.85 (dt, *J* = 10.8, 9.1 Hz, 1H), 1.74 (dddd, *J* = 10.7, 9.5, 3.3, 0.9 Hz, 1H), 1.39 (s, 3H), 1.14 (s, 3H).

^{13}C NMR δ 171.8, 148.3, 138.6, 136.4, 134.7, 128.1, 127.6, 121.7, 121.3, 116.4, 51.0, 40.4, 32.3, 30.9, 23.4, 17.4.

FTIR (NaCl, thin film) 3353, 3047, 2952, 2861, 1685, 1595, 1577, 1526, 1485, 1460, 1424, 1385, 1324, 1261, 1239, 1187, 1169, 1153, 825, 791,756 $cm.^{-1}$

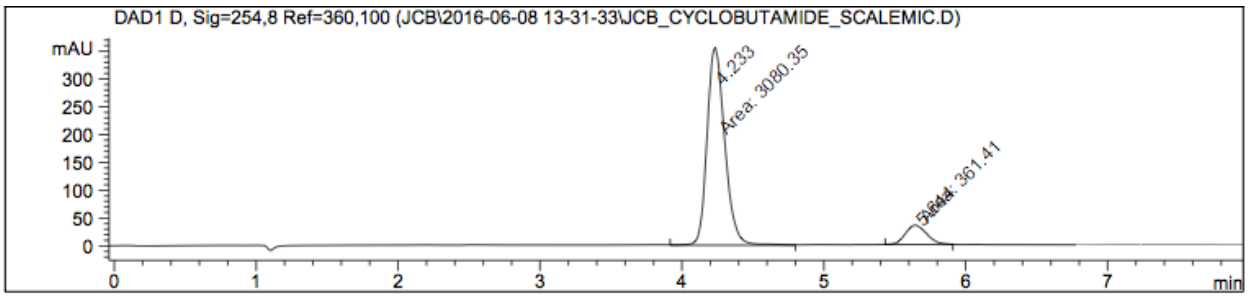
HRMS (MM) calc'd for $C_{16}H_{19}N_2O$ $[M+H]^+$ 255.1492, found 255.1501.

SFC data for racemic 5:



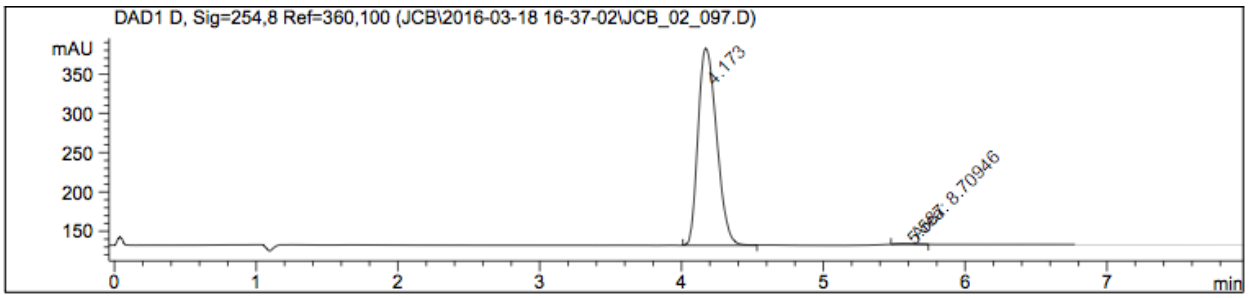
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.246	BB	0.1286	8934.03320	1078.74268	51.8271
2	5.660	BB	0.1532	8304.11426	855.84570	48.1729

Enantioenriched 5 isolated directly from reaction:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.233	MM	0.1444	3080.35034	355.58780	89.4993
2	5.644	MM	0.1739	361.41000	34.64573	10.5007

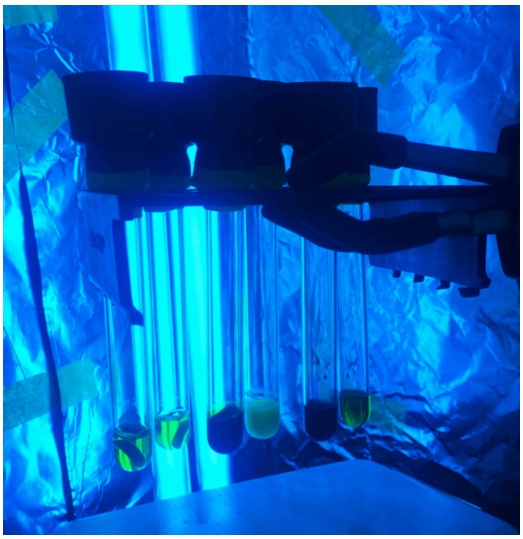
Enantiopure 5 after a single recrystallization:



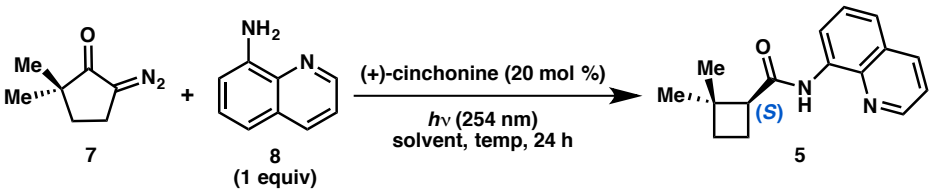
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.173	BB	0.1464	2285.16455	250.58836	99.6203
2	5.587	MM	0.1518	8.70946	9.55969e-1	0.3797

Small-scale screening protocol for cyclobutane 5.

Inside a N_2-filled glovebox, six oven-dried quartz tubes were charged with aminoquinoline (14.4 mg, 0.100 mmol, 1.00 equiv) and catalyst (20–50 mol %). Diazoketone **7** (13.8 mg, 0.100 mmol) was then added to each as a solution in 1.00 mL THF and the reactions fitted with a 19/38 rubber septum around the outside of each tube and sealed with electrical tape. The reactions were brought out of the glovebox and placed in a bottomless test tube rack in front of a Honeywell 254 nm lamp. The reactions were irradiated with stirring at room temperature for 24 hours. The reactions were then concentrated *in vacuo* and the crude reactions mixtures either analyzed by ^{1}H NMR with an added internal standard, or purified by silica gel flash chromatography (isocratic: 6% EtOAc/hexane) to provide **5** in varying yields and enantiopurities.



Additional experimental results for optimization of asymmetric Wolff rearrangement:

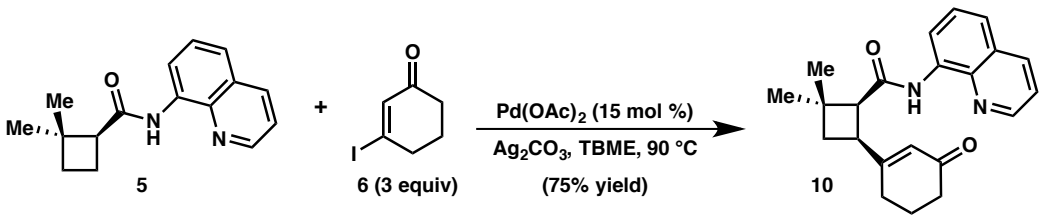


7 8 (1 equiv) 5

entry	solvent	temp °C	vessel	atm	% yield[a]	% ee[b]
1	THF	25	quartz	N_2	63	79
2	DMF	25	quartz	N_2	76	50
3	DCM	25	quartz	N_2	62	47
4	toluene	25	quartz	N_2	65	59
5	dioxane	25	quartz	N_2	69	79
6	MeCN	25	quartz	N_2	43	74
7	THF	0	quartz	N_2	28	79
8	THF	25	quartz	air	18	75
9	THF	25	quartz	CO	33	69
10	THF	25	vycor	N_2	29	79
11	THF	25	pyrex	N_2	20	75

[a] Determined by ^{1}H NMR via integration relative to an added internal standard.
[b] Determined by SFC using a chiral stationary phase.

Preparation of *cis*-cyclobutane 10.



5 6 (3 equiv) (75% yield) 10

To a flame-dried 150 mL pressure vessel were added cyclobutane **5** (2.87 g, 11.3 mmol), vinyl iodide **6**[4] (7.50 g, 33.8 mmol, 3.00 equiv), $Pd(OAc)_2$ (379 mg, 1.69 mmol, 0.150 equiv), and Ag_2CO_3 (3.11 g, 11.3 mmol, 1.00 equiv). The reagents were suspended in TBME (56.0 mL) and the vessel sealed under ambient conditions. The reaction was heated to 90 °C for 16 hours, then cooled to room temperature and filtered over a pad of celite. The filtrate was concentrated directly onto celite and purified by silica gel flash chromatography (20–40% EtOAc/hexane) to afford *cis*-cyclobutane **10** (2.95 g, 75%) as a pale yellow foam: $[\alpha]_D^{25.0}$ = +84.4° (c = 0.350, $CHCl_3$).

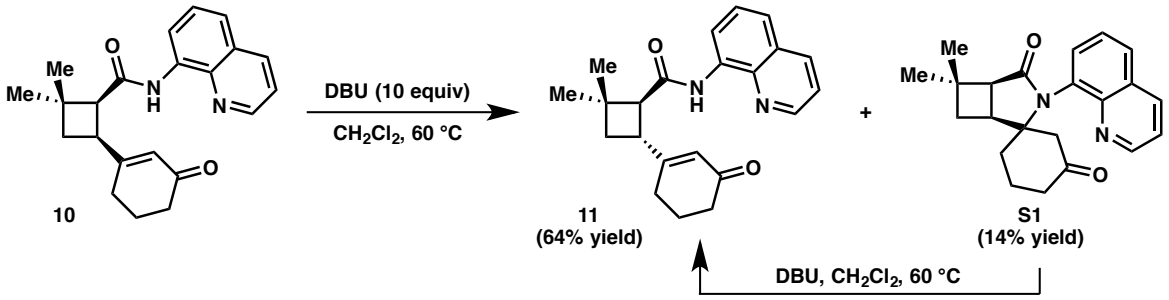
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.78 (dd, *J* = 12.4, 2.1 Hz, 1H), 8.78 (t, *J* = 1.8 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.51 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.50 (d, *J* = 0.9 Hz, 1H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.00 (q, *J* = 1.6 Hz, 1H), 3.45 (ddddd, *J* = 10.8, 8.5, 7.6, 2.1, 1.0 Hz, 1H), 3.27 (ddd, *J* = 8.8, 2.8, 0.8 Hz, 1H), 2.48 (t, *J* = 10.8 Hz, 1H), 2.31 (ddd, *J* = 7.5, 5.7, 3.5 Hz, 2H), 2.20 (qd, *J* = 6.0, 5.5, 1.1 Hz, 2H), 2.01 (ddd, *J* = 11.0, 8.3, 2.8 Hz, 1H), 1.95 – 1.84 (m, 2H), 1.46 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 170.2, 166.5, 148.3, 138.4, 136.3, 134.4, 127.9, 127.4, 124.9, 121.6, 121.5, 116.5, 56.9, 37.5, 37.5, 36.8, 35.7, 29.9, 27.8, 24.9, 22.6.

FTIR (NaCl, thin film) 3348, 2929, 2865, 1662, 1623, 1595, 1576, 1522, 1485, 1424, 1386, 1347, 1322, 1258, 1191, 1165, 1132, 827, 793 cm.$^{-1}$

HRMS (MM) calc'd for $C_{22}H_{25}N_2O_2$ $[M+H]^+$ 349.1911, found 349.1910.

Preparation of *trans*-cyclobutane 11 and spirolactam S1.



To a 150 mL pressure vessel were added *cis*-cyclobutane **10** (2.74 g, 7.86 mmol) and wet DCM (27.5 mL). The colorless solution was treated with DBU (11.7 mL, 78.6 mmol, 10.0 equiv) and a bright yellow color was observed immediately. The vessel was sealed under ambient conditions and heated to 60 °C for 20 hours. The reaction mixture was diluted with 100 mL of water and 100 mL of DCM. The layers were separated, and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (isocratic: 40% EtOAc/hexane until **11** eluted completely, then 10% MeOH/DCM) to afford **11** (1.74 g, 64% yield) and **S1** (367 mg, 14% yield), each as a pale yellow solid.

Data for *trans*-cyclobutane **11**: $[\alpha]_D^{25.0} = -129.0°$ (c = 1.43, $CHCl_3$).

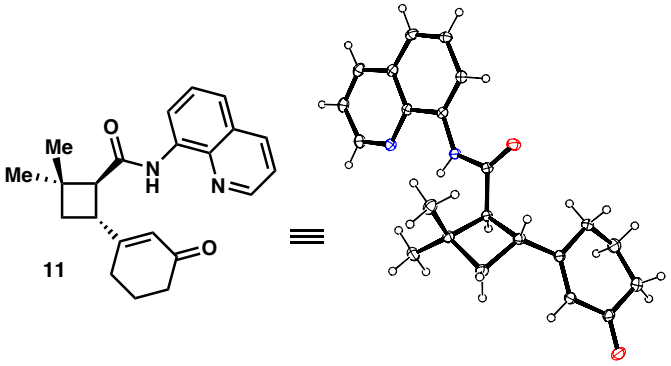
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.73 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.52 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.49 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.92 (q, *J* = 1.5 Hz, 1H), 3.58 (ddq, *J* = 18.5, 8.7, 1.6, 0.8, 0.8 Hz, 1H), 2.97 (dd, *J* = 9.8, 0.7 Hz, 1H), 2.41 – 2.29 (m, 4H), 2.05 – 1.92 (m, 3H), 1.85 (t, *J* = 10.4 Hz, 1H), 1.40 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 169.6, 167.5, 148.3, 138.3, 136.3, 134.2, 127.9, 127.3, 123.9, 121.7, 121.5, 116.3, 55.5, 37.5, 36.8, 36.4, 36.3, 30.7, 27.6, 23.1, 22.6.

FTIR (NaCl, thin film) 3344, 3046, 2952, 2865, 2246, 1669, 1623, 1595, 1577, 1526, 1485, 1461, 1424, 1323, 1346, 1326, 1292, 1253, 1191, 1161, 1133, 915, 884, 827, 792, 757,731 cm.$^{-1}$

HRMS (MM) calc'd for $C_{22}H_{25}N_2O_2$ $[M+H]^+$ 349.1911, found 349.1919.

XRCD: A suitable crystal of $C_{22}H_{24}N_2O_2$ (**11**) was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Cu-Kα radiation at a temperature of 120 K. Using Olex2, [5] the structure was solved with the ShelXS [6] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter, -0.04(4).



Data for spirolactam **S1**, 2.5:1 mixture of diastereomers: $[\alpha]_D^{25.0} = -56.5°$ (c = 1.085, $CHCl_3$).

^{1}H NMR (asterisk denotes minor diast., 400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.85* (dd, *J* = 4.1, 1.8 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.13* (dd, *J* = 8.3, 1.8 Hz, 1H), 7.87 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.49 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.37* (dd, *J* = 8.3, 4.1 Hz, 1H), 3.07* (ddd, *J* = 7.3, 3.2, 0.9 Hz, 1H), 2.93 (dd, *J* = 6.0, 3.3 Hz, 1H), 2.86 (d, *J* = 13.2 Hz, 1H), 2.83 – 2.73 (m, 1H), 2.53 (dt, *J* = 13.1, 2.4 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.27 (ddq, *J* = 15.1, 11.3, 2.1 Hz, 1H), 2.15 – 1.94 (m, 2H), 1.94 – 1.83 (m, 1H), 1.71 (dtd, *J* = 13.2, 8.6, 7.6, 3.0 Hz, 1H), 1.52 – 1.38* (m, 1H), 1.35 (s, 3H), 1.34* (s, 3H), 1.31 (s, 3H), 1.14* (s, 3H), 1.03 (td, *J* = 13.7, 4.0 Hz, 1H).

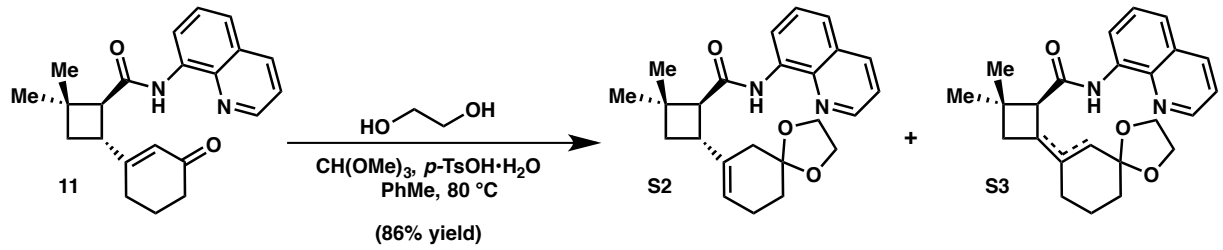
^{13}C NMR (major diastereomer, 101 MHz, $CDCl_3$) δ 209.2, 175.5, 150.7, 146.3, 136.1, 134.2, 130.7, 129.6, 129.1, 126.2, 121.9, 69.2, 53.2, 49.9, 40.7, 35.8, 34.8, 34.1, 30.2, 29.0, 25.6, 20.1.

^{13}C NMR (minor diastereomer, 101 MHz, $CDCl_3$) δ 210.0, 175.5, 150.7, 145.6, 136.0, 134.2, 131.5, 129.6, 129.2, 126.0, 121.7, 68.9, 52.9, 49.8, 40.4, 35.0, 34.8, 34.6, 31.3, 30.0, 26.1, 20.1.

FTIR (NaCl, thin film) 3356, 3039, 2953, 2933, 2866, 1705, 1687, 1616, 1596, 1574, 1525, 1496, 1472, 1426, 1391, 1341, 1312, 1279, 1250, 1223, 1134, 1124, 1038, 1027, 905, 831, 795, 753, 664, 643 cm.$^{-1}$

HRMS (MM) calc'd for $C_{22}H_{25}N_2O_2$ $[M+H]^+$ 349.1911, found 349.1916.

Preparation of dioxolanes S2 & S3.



To a flame-dried 200 mL round-bottom flask was added *trans*-cyclobutane **11** (2.59 g, 7.43 mmol) and the atmosphere was exchanged for N_2 three times. Dry PhMe (74 mL) was then added, followed by ethylene glycol (16.6 mL, 297 mmol, 40.0 equiv) and trimethyl orthoformate (2.44 mL, 22.3 mmol, 3.00 equiv) via syringe. Finally, *p*-toluenesulfonic acid monohydrate (141 mg, 0.743 mmol, 0.10 equiv) was added as a solid in one portion under a stream of N_2. The reaction mixture was heated to 80 ºC for 15 hours, at which point the reaction mixture was cooled to room temperature and quenched with a saturated solution of aqueous $NaHCO_3$. The layers were separated and the aqueous layer was extracted with EtOAc three times. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (isocratic: 20% EtOAc/hexane + 1% Et_3N) to afford dioxolanes **S2** and **S3** (2.50 g, 86% yield) as a partially separable mixture of inconsequential olefin isomers. An analytically pure sample of the major dioxlane (**S2**) was obtained and a representative spectrum of the mixture as used in the next step is also provided.

Data for **S2** (major product, peak 1): $[\alpha]_D^{25.0} = -80.5°$ (c = 1.40, $CHCl_3$)

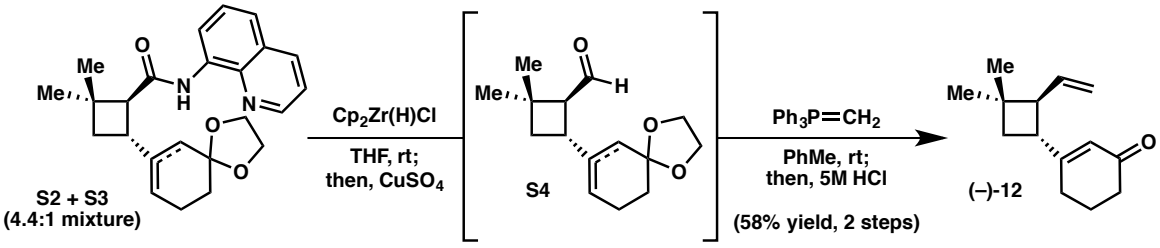
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.78 (dd, *J* = 11.0, 1.6 Hz, 1H), 8.78 (d, *J* = 1.6 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.50 (dt, *J* = 15.8, 8.2, 7.5 Hz, 2H), 7.47 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.54 (dt, *J* = 3.6, 1.8 Hz, 1H), 3.96 (q, *J* = 4.4, 3.9 Hz, 4H), 3.30 (q, *J* = 9.4 Hz, 1H), 2.88 (d, *J* = 9.8 Hz, 1H), 2.25 (d, *J* = 2.8 Hz, 4H), 1.87 (dd, *J* = 10.5, 8.6 Hz, 1H), 1.81 – 1.61 (m, 3H), 1.36 (s, 3H), 1.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 148.2, 138.4, 137.3, 136.3, 134.6, 127.9, 127.4, 121.6, 121.2, 119.1, 116.3, 108.4, 64.4, 55.2, 36.7, 36.7, 36.4, 36.1, 30.9, 30.8, 24.1, 23.4.

FTIR (NaCl, thin film) 3350, 3046, 2952, 2929, 2893, 2839, 1686, 1596, 1578, 1525, 1485, 1460, 1424, 1383, 1368, 1326, 1248, 1209, 1161, 1102, 1059, 1021, 948, 826, 792, 756 cm.$^{-1}$

HRMS (MM) calc'd for $C_{24}H_{29}N_2O_3$ $[M+H]^+$ 393.2173, found 393.2188.

Preparation of vinyl enone (–)-12.



Inside a N_2-filled glovebox, two flame-dried 200 mL round-bottom flasks were each charged with Schwartz's reagent (1.60 g, 6.21 mmol, 2.04 equiv) and sealed under N_2. The flasks were removed from the glovebox and THF (15.5 mL) was added to each via syringe. To each of the milky-white suspensions was added a mixture of dioxolanes **S2** and **S3** (1.19 g, 3.04 mmol) as a solution in THF (16.0 mL) in a quick drip at room temperature. The mixtures immediately began to turn yellow, darkening to orange over the course of 1 hour, at which point the reactions were quenched with saturated aqueous $NaHCO_3$ and combined together. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed twice with 100 mL of a 0.6M aqueous solution of $CuSO_4$ to remove the liberated 8-aminoquinoline. The organic layer was then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude aldehyde (**S4**, 1.70 g) was dissolved in dry PhMe (20 mL) and treated with freshly prepared ylide (80 mL, 32.0 mmol, 5.26 equiv) at room temperature. The reaction was stirred for 2 hours and monitored by TLC. Upon complete conversion, the reaction was cooled to 0 °C and quenched with 5 M HCl. The layers were separated and the aqueous layer was extracted twice with Et_2O. The combined organic layers were concentrated *in vacuo* and the solvent replaced with THF (30 mL). The dioxolane was hydrolyzed by stirring vigorously with 5 M HCl for 8 hours, at which time Et_2O was added and the layers separated. The aqueous layer was extracted twice with Et_2O and the combined organics washed with aqueous $NaHCO_3$, dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (isocratic: 30% Et_2O/hexanes) to afford vinyl enone (–)-**12** (715 mg, 58% yield over 2 steps) as a clear oil: $[\alpha]_D^{25.0} = -100°$ (c = 1.02, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (q, *J* = 1.5 Hz, 1H), 5.81 (dddt, *J* = 16.8, 10.6, 7.9, 0.5, 0.5 Hz, 1H), 5.04 (qd, *J* = 1.9, 1.0 Hz, 1H), 5.01 (ddd, *J* = 10.4, 2.0, 1.1 Hz, 1H), 2.88 (q, *J* = 9.7, 9.1, 9.0 Hz, 1H), 2.48 (ddq, *J* = 9.8, 7.9, 1.0 Hz, 1H), 2.34 (t, *J* = 7.0, 6.5 Hz, 2H), 2.21 (qdd, *J* = 5.9, 1.5, 0.8 Hz, 2H), 1.95 (dt, *J* = 7.7, 6.1 Hz, 2H), 1.85 (ddd, *J* = 10.7, 8.3, 0.8 Hz, 1H), 1.67 (t, *J* = 10.4 Hz, 1H), 1.05 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 168.7, 137.4, 123.4, 116.1, 53.8, 41.1, 37.5, 37.3, 36.0, 30.0, 27.9, 23.1, 22.6.

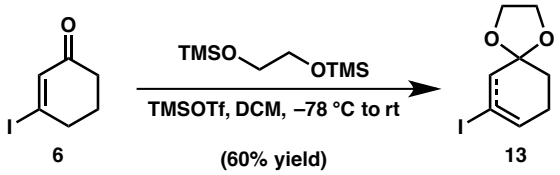
FTIR (NaCl, thin film) 3320, 3076, 3039, 2953, 2934, 2891, 2866, 2827, 1671, 1622, 1456, 1428, 1417, 1382, 1368, 1346, 1324, 1290, 1251, 1191, 1124, 995, 968, 942, 912, 886, 755 $cm.^{-1}$

HRMS (MM) calc'd for $C_{14}H_{21}O$ $[M+H]^+$ 205.1587, found 205.1587.

Preparation of Wittig ylide.

Inside a N_2-filled glovebox, methyltriphenylphosphonium bromide (22.2 g, 62.1 mmol) and KO*t*-Bu (7.36 g, 65.6 mmol, 1.06 equiv) were added to a flame-dried 500 mL round-bottom flask and sealed under nitrogen. The flask was brought out of the box and dry PhMe (155 mL) was added via syringe. The flask was fitted with a reflux condenser under a stream of N_2 and heated to 110 °C for 4 hours, at which time the reaction was cooled to room temperature and the salts were allowed to settle for 3 hours before the bright yellow supernatant (~0.40 M salt-free ylide) was used for the methylenation of crude *trans*-aldehyde **S4,** as well as purified *cis/trans*-aldehyde **S5**.

Preparation of protected iodide 13.



Inside a N_2-filled glove box, a 250 mL round bottom flask was charged with TMSOTf (0.410 mL, 0.230 mmol, 0.010 equiv) and DCM (20.0 mL). The flask was sealed, removed from the glove box, and placed under a N_2 atmosphere. The reaction mixture was cooled to –78 ºC, and 1,2-bistrimethylsilyloxyethane (11.0 mL, 45.0 mmol, 2.00 equiv) was added via syringe. (Note, best results were obtained when 1,2-bistrimethylsilyloxyethane was sparged with argon for 30 min prior to addition). Vinyl iodide **6** (5.00 g, 22.5 mmol, 1.00 equiv) was added to the flask dropwise as a solution in DCM (20.0 mL), via cannula transfer. An additional portion of DCM (5.00 mL) was used to complete the transfer. The colorless reaction mixture was allowed to stir at –78 ºC for 1 hour, at which point the reaction mixture was warmed to 0 ºC. The reaction mixture became yellow immediately upon warming and was allowed to warm to room temperature over 16 hours. The reaction mixture became dark orange and was quenched with the addition of DIPEA (11.0 mL), at which point the reaction became yellow. The mixture was poured into a separatory funnel and diluted with saturated $NaHCO_3$ solution. The aqueous layer was extracted three times with DCM. The organic layers were combined, dried over a 1:1 mixture of anhydrous K_2CO_3 and Na_2SO_4, filtered, and concentrated to provide a yellow residue that was purified by flash silica gel chromatography (5% EtOAc, 1% Et_3N/hexane – 20% EtOAc, 1% Et_3N/hexane) to provide **13** (3.61 g, 60% yield) as a 8:1 mixture of olefin isomers, as a pale yellow oil.

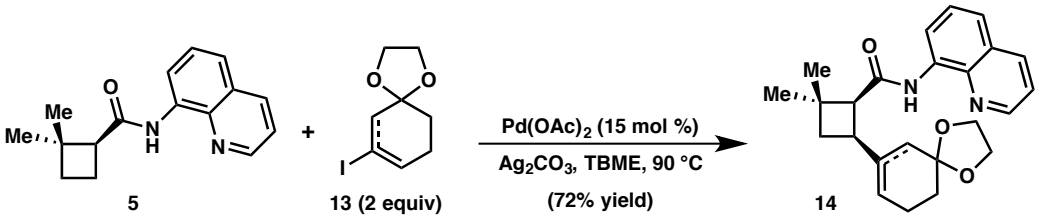
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (tt, *J* = 4.0, 1.9 Hz, 1H), 3.98 (p, *J* = 1.7 Hz, 4H), 2.72 (q, *J* = 2.3 Hz, 2H), 2.36 – 2.22 (m, 2H), 1.77 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 108.1, 91.1, 64.7, 49.3, 30.2, 27.5.

FTIR (NaCl, thin film) 3040, 2955, 2934, 2881, 2836, 2684, 1637, 1474, 1443, 1429, 1418, 1360, 1330, 1300, 1243, 1207, 1142, 1114, 1076, 1058, 1021, 970, 948, 889, 848, 827, 776, 738, 662 cm.$^{-1}$

HRMS (FAB) calc'd for $C_8H_{11}IO_2$ $[M]^+$ 266.9876, found 266.9888.

Preparation of *cis*-dioxolane 14.



A 100 mL, thick-walled pressure vessel was charged with $Pd(OAc)_2$ (132 mg, 0.590 mmol, 0.150 equiv), Ag_2CO_3 (1.08 g, 3.93 mmol, 1.00 equiv), and **5** (1.00 g, 3.93 mmol, 1.00 equiv). Vinyl iodide **13** (2.09 g, 7.86 mmol, 2.00 equiv) was then added to the flask as a solution in TBME (19.7 mL). The reaction vessel was sealed with a screw top under ambient conditions and heated to 90 ºC in an oil bath. The heterogeneous reaction mixture is olive green upon addition of vinyl iodide. After heating for five minutes, the reaction mixture became black. After 16 hours, the flask was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was filtered over a pad of celite and the filter cake was washed with DCM. The filtrate was concentrated, and the crude orange residue was purified by flash silica gel chromatography (30% EtOAc, 1% Et_3N/hexane–35% EtOAc, + 1% Et_3N/hexane) to provide **14** (1.11 g, 72% yield) as a white foam: $[\alpha]_D^{25.0} = -29.3°$ (c = 1.95, $CHCl_3$).

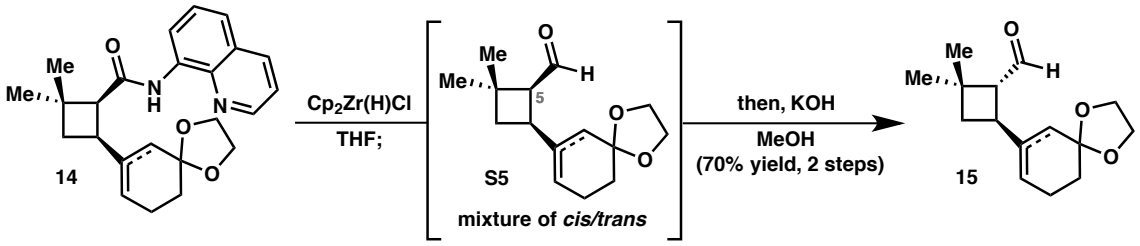
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.81 (ddd, *J* = 24.2, 7.3, 1.5 Hz, 2H), 8.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.49 (td, *J* = 8.2, 7.5, 6.6 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.65 (dd, *J* = 17.8, 9.1 Hz, 1H), 4.03 – 3.81 (m, 2H), 3.76 – 3.64 (m, 2H), 3.25 (q, *J* = 9.1, 8.2 Hz, 1H), 3.05 (dd, *J* = 8.7, 2.8 Hz, 1H), 2.46 (t, *J* = 10.9 Hz, 1H), 2.40 – 2.23 (m, 2H), 2.19 (dt, *J* = 16.5, 2.1 Hz, 1H), 2.06 – 1.97 (m, 1H), 1.93 (ddd, *J* = 11.1, 8.3, 2.9 Hz, 1H), 1.71 – 1.59 (m, 1H), 1.57 – 1.48 (m, 1H), 1.40 (s, 3H), 1.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 147.9, 138.7, 136.3, 134.9, 134.8, 127.9, 127.5, 121.4, 121.2, 120.8, 116.6, 108.3, 64.3, 64.1, 55.9, 37.2, 37.1, 36.7, 35.4, 30.8, 30.2, 25.1, 24.4.

FTIR (NaCl, thin film) 3357, 3300, 3043, 3006, 2952, 2928, 2881, 1685, 1664, 1596, 1577, 1523, 1485, 1460, 1424, 1385, 1324, 1255, 1208, 1160, 1132, 1106, 1060, 1039, 1020, 947, 846, 826, 792, 755, 666 $cm.^{-1}$

HRMS (MM) calc'd for $C_{24}H_{29}N_2O_3$ $[M+H]^+$ 393.2173, found 393.2183.

Preparation of *trans*-aldehyde (15).



Inside a N_2-filled glove box, a 250 mL round bottom flask was charged with Schwartz's reagent (2.30 g, 8.92 mmol, 2.06 equiv) and THF (22.3 mL). *Cis*-dioxolane **14** (1.70 g, 4.32 mmol, 1.00 equiv) was added to the flask as a solution in THF (22.3 mL). The flask was sealed, removed from the glove box and put under a N_2 atmosphere. The flask was covered with aluminum foil and allowed to stir for one hour, at which point the reaction was quenched with the addition of saturated $NaHCO_3$ solution. (Note, it is important that the quench be conducted very quickly to avoid decomposition of excess Schwartz's reagent and formation of HCl). The reaction mixture was diluted with EtOAc and the organic layer separated. The aqueous layer was filtered through a pad of celite and sand and then extracted 5x with EtOAc. The combined organics were dried over anhydrous Na_2SO_4, filtered, and concentrated to provide a yellow residue that was purified by flash silica gel chromatography (15% EtOAc, 1% Et_3N/hexanes) to provide **S5** (755 mg, 3.01 mmol) as a yellow oil as a 1.8:1 (*cis*/*trans*) mixture of diastereomers at C5. The oil was concentrated directly into a 200 mL round bottom flask and dissolved in wet MeOH (60.0 mL). The flask was then charged with KOH (3.36 g, 59.9 mmol, 20.0 equiv) and the mixture allowed to stir for 1 hour at room temperature. The mixture was then concentrated to a volume of ~3 mL and diluted with pH 7 buffer. A pale yellow precipitate formed upon addition of buffer. The solution was slowly acidified using dilute citric acid until pH 7 was achieved. The mixture was then poured into a separatory funnel and extracted 3x with EtOAc. The combined organics were dried over anhydrous Na_2SO_4, filtered, and concentrated to provide *trans*-aldehyde **15** (755 mg, 70% over 2 steps) as a mixture of olefin isomers. The yellow oil was analytically pure and used directly in the next step: $[\alpha]_D^{25.0}$ = +35.2° (c = 0.295, $CHCl_3$). Note: it is recommended that the aldehyde be used immediately in the next step to avoid decomposition.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 2.2 Hz, 1H), 5.37 (dt, *J* = 3.8, 1.9 Hz, 1H), 3.97 (dd, *J* = 2.5, 1.3 Hz, 4H), 3.14 (q, *J* = 9.2 Hz, 1H), 2.73 (dt, *J* = 10.0, 2.1 Hz, 1H), 2.22 (dp, *J* = 6.5, 2.1 Hz, 2H), 2.16

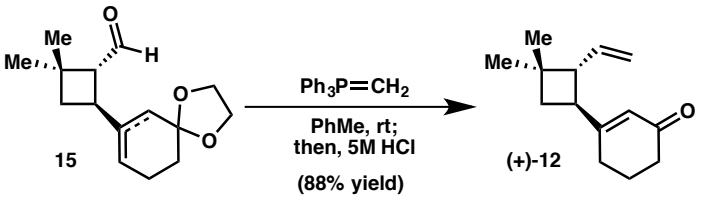
– 1.97 (m, 2H), 1.77 (ddd, *J* = 15.5, 9.4, 2.0 Hz, 2H), 1.69 (td, *J* = 6.5, 2.1 Hz, 2H), 1.24 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 137.1, 118.8, 108.3, 64.4, 59.5, 37.3, 37.1, 36.7, 34.3, 31.2, 30.7, 24.0, 24.0.

FTIR (NaCl, thin film) 2954, 2929, 2896, 2873, 2707, 1712, 1670, 1577, 1522, 1461,1449, 1434, 1420, 1383, 1367, 1340, 1312, 1297, 1249, 1209, 1179, 1103, 1059, 1039, 1018, 948, 846, 793 cm.$^{-1}$

HRMS (MM) calc'd for $C_{15}H_{23}O_3$ $[M+H]^+$ 251.1642, found 251.1645.

Preparation of vinyl enone (+)-12



A 250 mL round bottom flask was charged with aldehyde, **15** (720 mg, 2.88 mmol, 1.00 equiv). The flask was evacuated and backfilled three times with N_2 and charged with toluene (2.30 mL). The flask was then charged with freshly prepared ylide solution[7] (36.0 mL, 0.4 M, 5.00 equiv) and the reaction mixture was allowed to stir for 30 minutes at room temperature. The reaction was quenched with the addition of saturated $NaHCO_3$ solution (10.0 mL). The organic layer was separated and the aqueous layer extracted 3x with Et_2O. The combined organics were concentrated and dissolved in a 1:1 mixture of THF and 5 M HCl (28 mL.0). The reaction mixture was allowed to stir over 16 hours, at which point the mixture was diluted with Et_2O and water. The layers were separated and the aqueous layer extracted 3x with Et_2O. The combined organics were dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude yellow residue was purified by flash silica gel chromatography (20–30% Et_2O/pentane) to provide (+)-**12** (520 mg, 88%) as a pale yellow oil: $[\alpha]_D^{25.0}$ = +102° (c = 0.705, $CHCl_3$).

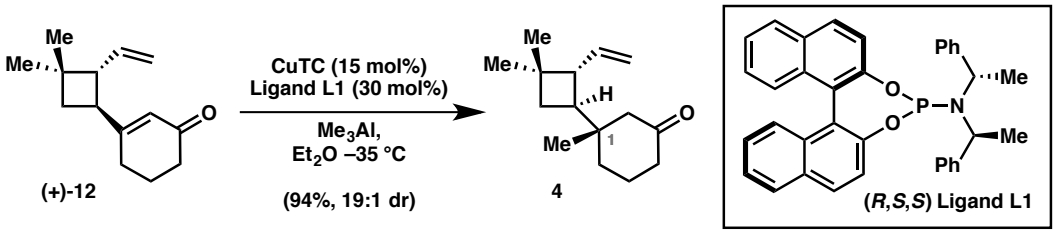
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (q, *J* = 1.6 Hz, 1H), 5.81 (dddt, *J* = 16.8, 10.6, 7.9, 0.5, 0.5 Hz, 1H), 5.04 (qd, *J* = 1.9, 1.0 Hz, 1H), 5.01 (ddd, *J* = 10.8, 1.9, 1.1 Hz, 1H), 2.88 (q, *J* = 9.7, 9.1, 9.0 Hz, 1H), 2.48 (ddq, *J* = 9.8, 7.9, 1.0 Hz, 1H), 2.34 (t, *J* = 7.0, 6.5 Hz, 2H), 2.20 (qdd, *J* = 6.0, 1.5, 0.8 Hz, 2H), 1.95 (dt, *J* = 7.7, 6.1 Hz, 2H), 1.85 (ddd, *J* = 10.8, 8.3, 0.8 Hz, 1H), 1.67 (t, *J* = 10.3 Hz, 1H), 1.05 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 168.8, 137.4, 123.4, 116.1, 53.8, 41.1, 37.5, 37.3, 36.0, 30.0, 27.9, 23.1, 22.6.

FTIR (NaCl, thin film) 3320, 3076, 3039, 2953, 2934, 2891, 2866, 2827, 1671, 1622, 1456, 1428, 1417, 1382, 1368, 1346, 1324, 1290, 1251, 1191, 1124, 995, 968, 942, 912, 886, 755 cm.$^{-1}$

HRMS (MM) calc'd for $C_{14}H_{21}O$ $[M+H]^+$ 205.1587, found 205.1587.

Preparation of vinyl ketone 4.



Inside a N_2-filled glovebox, CuTC (105 mg, 0.551 mmol, 0.150 equiv) and (*R*,*S*,*S*)-ligand **L1**[8] (594 mg, 1.10 mmol, 0.30 equiv) were added to a flame dried 100 mL round-bottom flask. The reagents were suspended in Et_2O (18.0 mL) and stirred at room temperature for 30 minutes before vinyl enone (+)-**12** (750 mg, 3.67 mmol) was added as a solution in Et_2O (18.0 mL). The reaction was sealed under N_2, removed from the glovebox and placed under a balloon atmosphere of argon. The reaction mixture was allowed to equilibrate to –35 °C for 5 minutes using a cryocool unit to maintain the temperature. Me_3Al (2.0 M in heptane; 3.67 mL, 7.34 mmol, 2.00 equiv) was then added dropwise and the reaction stirred at –35 °C for 17 hours, at which point wet MeOH (5 mL) was slowly added to quench excess Me_3Al. The mixture was warmed to room temperature, filtered over a plug of silica gel and washed thoroughly with Et_2O and DCM (until no product remained in eluent). The filtrate was concentrated *in vacuo* and the crude residue purified by silica gel flash chromatography (isocratic: 20% hexane/DCM) to afford vinyl ketone **4** (760 mg, 94% yield) as a 19:1 mixture of inseparable diastereomers at C1, colorless oil. Note: this 19:1 mixture is carried through the next three reactions, and a single diastereomer at C1 is isolable after the ring-closing metathesis: $[\alpha]_D^{25.0}$ = +37.6° (c = 1.05, $CHCl_3$).

^{1}H NMR (400 MHz, C_6D_6) δ 5.68 (ddd, *J* = 16.9, 10.5, 8.6 Hz, 1H), 4.96 (qd, *J* = 2.2, 0.8 Hz, 1H), 4.93 (ddd, *J* = 11.3, 2.2, 0.8 Hz, 1H), 2.20 (ddt, *J* = 9.6, 8.6, 0.9 Hz, 1H), 2.11 (dtt, *J* = 13.9, 4.8, 1.4 Hz, 1H), 1.92 (dd, *J* = 3.3, 1.7 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.50 – 1.40 (m, 2H), 1.31 – 1.21 (m, 2H), 1.21 – 1.13 (m, 1H), 0.99 (dtt, *J* = 13.4, 4.7, 4.5, 1.5, 1.1 Hz, 1H), 0.94 (s, 3H), 0.93 (s, 3H), 0.66 (s, 3H).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddd, *J* = 17.1, 10.3, 8.7 Hz, 1H), 5.08 – 4.81 (m, 2H), 2.33 (ddd, *J* = 9.6, 8.7, 0.9 Hz, 1H), 2.30 – 2.19 (m, 2H), 2.16 (d, *J* = 13.5 Hz, 1H), 2.07 (td, *J* = 10.1, 8.5 Hz, 1H), 1.99

(dt, *J* = 13.4, 1.8 Hz, 1H), 1.90 (ddq, *J* = 14.0, 6.2, 4.7 Hz, 1H), 1.85 – 1.72 (m, 1H), 1.56 (ddd, *J* = 13.6, 11.1, 4.4 Hz, 1H), 1.51 – 1.34 (m, 3H), 0.98 (s, 3H), 0.97 (s, 3H), 0.83 (s, 3H).

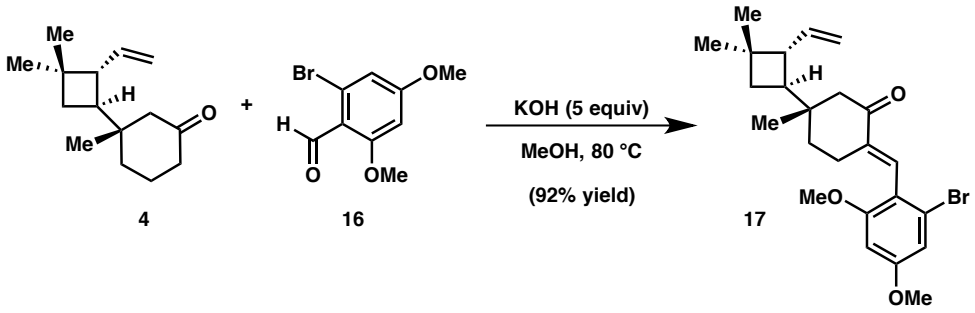
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8, 139.6, 115.3, 51.2, 49.5, 45.2, 41.3, 40.1, 34.8, 34.0, 33.0, 30.1, 23.7, 22.1, 21.8.

^{13}C NMR (101 MHz, C_6D_6) δ 209.3, 139.9, 115.3, 51.0, 49.5, 45.2, 41.2, 39.7, 34.7, 33.9, 32.9, 30.1, 23.7, 22.1, 21.8.

FTIR (NaCl, thin film) 3075, 2953, 2873, 1713, 1633, 1460, 1422, 1382, 1368, 1312, 1285, 1253, 1228, 1172, 1049, 995, 910 cm.$^{-1}$

HRMS (FAB) calc'd for $C_{15}H_{24}O$ $[M]^+$ 221.1900, found 221.1897.

Preparation of *exo*-enone 17.



To a 200 mL round-bottom flask were added vinyl ketone **4** (884 mg, 4.01 mmol), aryl aldehyde **16**[9] (1.08 g, 4.41 mmol, 1.10 equiv), and KOH (1.13 g, 20.1 mmol, 5.00 equiv). Freshly distilled MeOH (40.1 mL) was then added, the flask fitted with a reflux condenser under ambient conditions and heated to 80 °C for 12 hours. At completion, the volume of MeOH was reduced *in vacuo* and the reaction quenched with a saturated solution of aqueous NH_4Cl. Et_2O was added and the layers were separated. The aqueous layer was extracted twice with Et_2O and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (isocratic: 20% Et_2O/hexane) to afford *exo*-enone **17** (1.66 g, 92% yield) as an off-white solid: $[\alpha]_D^{25.0}$ = +11.4° (c = 1.08, $CHCl_3$).

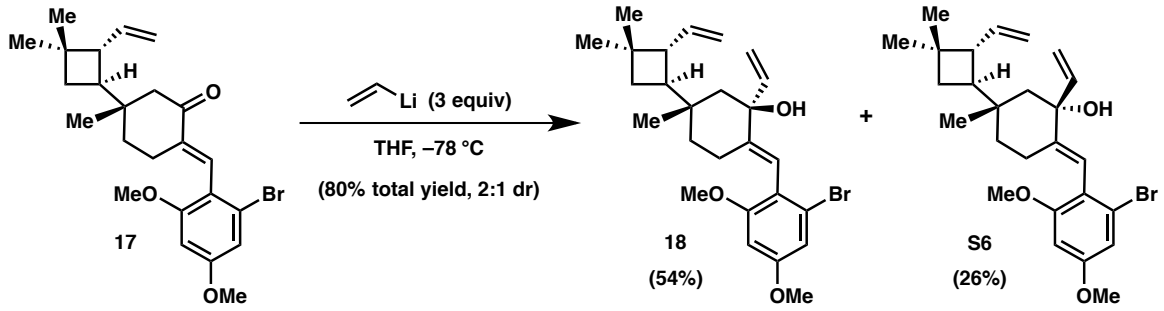
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 6.40 (d, *J* = 2.3 Hz, 1H), 5.74 (ddd, *J* = 17.1, 10.3, 8.6 Hz, 1H), 4.95 (ddd, *J* = 24.7, 2.1, 0.8 Hz, 1H), 4.94 (td, *J* = 2.3, 0.8 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 2.44 – 2.20 (m, 5H), 2.12 (td, *J* = 10.0, 8.5 Hz, 1H), 1.55 (ddd, *J* = 13.3, 10.3, 6.0 Hz, 1H), 1.50 (ddd, *J* = 10.7, 8.4, 0.6 Hz, 1H), 1.45 (d, *J* = 10.4 Hz, 1H), 1.38 (dtd, *J* = 11.0, 5.0, 2.1 Hz, 1H), 0.99 (s, 3H), 0.98 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 160.8, 158.6, 139.6, 139.2, 130.5, 125.1, 118.7, 115.3, 109.0, 98.1, 55.8, 55.7, 50.3, 49.4, 45.0, 36.5, 34.9, 33.2, 32.5, 30.1, 24.7, 23.7, 22.6.

FTIR (NaCl, thin film) 3073, 3000, 2952, 2863, 1686, 1599, 1558, 1482, 1461, 1435, 1407, 1381, 1367, 1303, 1259, 1214, 1153, 1051, 1035, 996, 938, 911, 960, 831, 795 cm.$^{-1}$

HRMS (MM) calc'd for $C_{24}H_{32}BrO_3$ $[M+H]^+$ 447.1529, found 447.1520.

Preparation of allylic alcohols 18 and S6.



A 100 mL round-bottom flask was flame dried under vacuum and backfilled with N_2. Dry THF (21.2 mL) was then added, followed by freshly prepared vinyllithium as a solution in THF (8.42 mL, 0.756 M, 3.00 equiv). The solution was cooled to –78 °C and *exo*-enone **17** (928 mg, 2.07 mmol) was taken up in 5.0 mL THF and added dropwise over 5 minutes. After 40 minutes, the reaction was quenched with a saturated solution of NH_4Cl and warmed to room temperature. The mixture was diluted with Et_2O and the layers were separated. The aqueous layer was extracted twice with Et_2O and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (30% hexane/DCM + 1% EtOAc until unreacted **17** and **S6** elute, then 5% EtOAc/DCM) to afford **18** (536 mg, 54%), **S6** (260 mg, 26%), and recovered **17** (164 mg, 18%).

Preparation of vinyllithium:

THF (38.0 mL) was added to a flame-dried 200 mL round-bottom flask under N_2, followed by tetravinyl tin (2.10 mL, 11.5 mmol). The solution was cooled to –78 °C and *n*-BuLi (17.3 mL, 2.5 M in hexanes, 43.3 mmol, 3.76 equiv) was added dropwise. The reaction was stirred for 20 minutes at –78 °C, then lifted out of the ice bath and allowed to warm to room temperature. The reaction was allowed to stir at room temperature for at least 2 hours before use, provides a ~0.756 M solution of vinyllithium (note: highest yields for 1,2-addition are obtained after stirring for 6 hours, at which time the mixture should be slightly milky grey in appearance).

Data for **18** (major diastereomer, peak 2): $[\alpha]_D^{25.0}$ = –23.8° (c = 1.07, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 2.3 Hz, 1H), 6.40 (d, *J* = 2.3 Hz, 1H), 6.19 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.04 (d, *J* = 1.5 Hz, 1H), 5.77 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H), 5.46 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.21 (dd, *J* = 10.6, 1.5 Hz, 1H), 4.92 (dddd, *J* = 17.0, 14.0, 2.2, 0.8 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 2.40 – 2.22 (m, 2H), 2.07 (q, *J* = 9.6 Hz, 1H), 1.92 (dt, *J* = 14.3, 4.5 Hz, 1H), 1.51 (q, *J* = 14.0, 13.3 Hz, 2H), 1.44 (d, *J* = 12.7 Hz, 1H), 1.41 (d, *J* = 9.4 Hz, 2H), 1.35 – 1.17 (m, 2H), 1.12 (s, 3H), 0.97 (d, *J* = 1.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 158.3, 146.6, 145.3, 140.5, 125.3, 120.4, 119.7, 114.8, 112.9, 108.5, 98.1, 76.1, 55.8, 55.7, 49.3, 47.0, 46.1, 34.7, 34.6, 34.4, 33.1, 30.0, 23.8, 23.4, 22.9.

FTIR (NaCl, thin film) 3424 (br) 3001, 2950, 2930, 2858, 2832, 1599, 1560, 1483, 1459, 1434, 1406, 1379, 1366, 1301, 1268, 1210, 1145, 1053, 1037, 994, 910, 879, 830, 811 cm.$^{-1}$

HRMS (MM) calc'd for $C_{26}H_{34}BrO_2$ $[M–OH]^+$ 457.1742, found 457.1744.

Data for **S6** (minor diastereomer, peak 1): $[\alpha]_D^{25.0}$ = –34.2° (c = 1.03, $CHCl_3$).

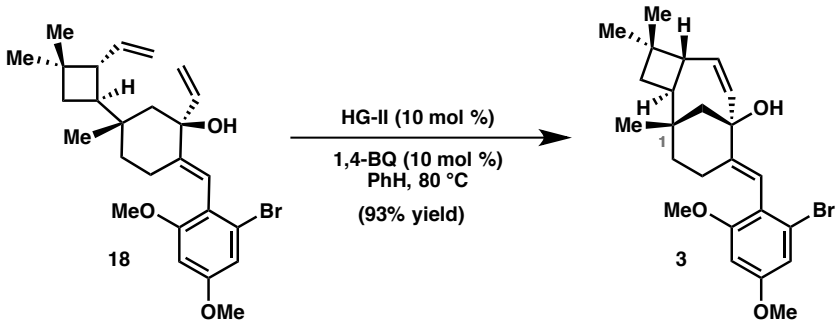
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 2.4 Hz, 1H), 6.42 (d, *J* = 2.3 Hz, 1H), 6.23 (d, *J* = 1.4 Hz, 1H), 6.09 (dd, *J* = 17.4, 10.3 Hz, 1H), 5.77 (ddd, *J* = 17.2, 10.2, 8.7 Hz, 1H), 5.48 (dd, *J* = 17.4, 1.5 Hz, 1H), 5.16 (dd, *J* = 10.3, 1.5 Hz, 1H), 4.93 (dddd, *J* = 18.0, 15.2, 2.2, 0.8 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 2.35 (t, *J* = 9.3 Hz, 1H), 2.15 – 2.02 (m, 2H), 1.90 (dddd, *J* = 14.3, 12.8, 4.4, 1.6 Hz, 1H), 1.77 – 1.65 (m, 2H), 1.59 (d, *J* = 13.2 Hz, 1H), 1.49 – 1.41 (m, 2H), 1.34 (td, *J* = 12.8, 4.3 Hz, 1H), 1.11 (dtd, *J* = 12.6, 4.0, 1.9 Hz, 1H), 0.97 (d, *J* = 1.1 Hz, 6H), 0.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 158.4, 146.2, 144.9, 140.6, 125.4, 120.9, 117.9, 115.6, 114.8, 108.4, 98.1, 75.8, 55.8, 55.7, 49.6, 49.1, 46.5, 35.6, 34.9, 34.5, 33.1, 30.1, 25.0, 23.8, 22.3.

FTIR (NaCl, thin film) 3451 (br) 3073, 2998, 2951, 2934, 2858, 1630, 1560, 1560, 1482, 1461, 1434, 1406, 1380, 1366, 1301, 1266, 1211, 1150, 1038, 996, 936, 909, 884, 830, 813 cm.$^{-1}$

HRMS (MM) calc'd for $C_{26}H_{34}BrO_2$ $[M–OH]^+$ 457.1742, found 457.1744.

Preparation of aryl bromide 3.



A 250 mL round-bottom flask containing allylic alcohol **18** (807 mg, 1.70 mmol) was pumped into a N_2-filled glovebox where Hoveyda–Grubbs second-generation catalyst (106 mg, 0.170 mmol, 0.100 equiv) and 1,4-benzoquinone (18.4 mg, 0.170 mmol, 0.100 equiv) were added. The flask was sealed under nitrogen, removed from the glovebox and dry benzene (85.0 mL) was added via syringe. The green reaction mixture was heated to 80 °C for 12 hours, then cooled to room temperature. Ethyl vinyl ether was added to inactivate the catalyst and stirred for 15 minutes before the reaction mixture was concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (20–30% Et_2O/hexane) to afford aryl bromide **3** (704 mg, 93%) as a white foam and a single diastereomer at C1: $[\alpha]_D^{25.0}$ = +95.5° (c = 0.815, $CHCl_3$).

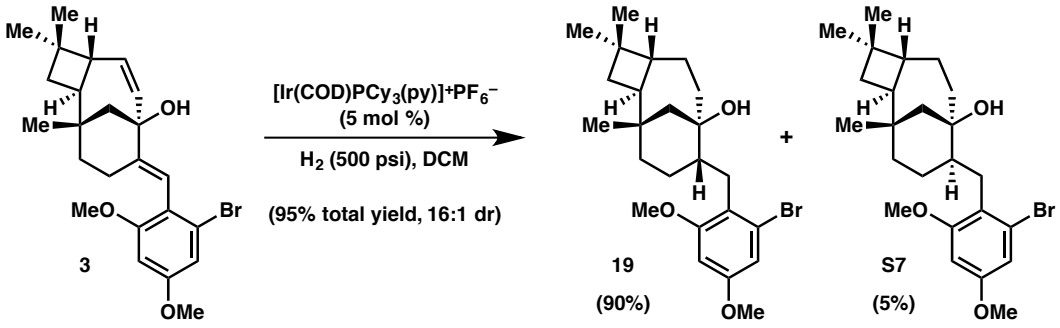
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 2.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 6.32 (d, *J* = 1.7 Hz, 1H), 5.84 (dd, *J* = 10.8, 2.4 Hz, 1H), 5.34 (ddd, *J* = 10.8, 2.8, 2.1 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 2.53 (dt, *J* = 11.6, 2.6 Hz, 1H), 2.37 (td, *J* = 11.2, 7.9 Hz, 1H), 2.28 (dd, *J* = 12.8, 2.3 Hz, 1H), 2.18 (dddd, *J* = 15.1, 11.0, 6.0, 1.9 Hz, 1H), 2.08 (ddd, *J* = 15.1, 5.2, 3.6 Hz, 1H), 1.75 (s, 1H), 1.60 – 1.46 (m, 2H), 1.41 (dd, *J* = 12.9, 2.2 Hz, 1H), 1.37 – 1.22 (m, 2H), 1.08 (s, 3H), 1.06 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 158.5, 147.7, 134.6, 131.6, 125.5, 120.8, 116.3, 108.5, 98.2, 76.7, 55.9, 55.7, 50.9, 45.4, 43.4, 38.3, 37.5, 35.1, 32.3, 30.9, 26.2, 24.5, 21.5.

FTIR (NaCl, thin film) 3422 (br) 3002, 2949, 2930, 2862, 1599, 1562, 1481, 1462, 1455, 1434, 1405, 1366, 1302, 1267, 1211, 1149, 1037, 1015, 979, 938, 870, 858, 830, 813, 772, 755 cm.$^{-1}$

HRMS (MM) calc'd for $C_{24}H_{30}BrO_2$ $[M–OH]^+$ 429.1429, found 429.1429.

Preparation of tertiary alcohols 19 and S7.



Inside a N_2-filled glovebox, Crabtree's catalyst (59.6 mg, 0.074 mmol, 0.05 equiv) was added to a 100 mL round-bottom flask containing bromide **3** (663 mg, 1.48 mmol). DCM (14.8 mL) was added and the flask was placed inside a steel bomb, which was closed under nitrogen and brought out of the glovebox. The pressure gauge was quickly attached and all bolts on the bomb tightened with a wrench. The bomb was connected to a H_2 inlet and the vessel purged with 250 psi H_2 three times before being charged to 500 psi. The reaction was stirred at room temperature for 3 hours, at which time H_2 was vented from the reaction. DCM was removed *in vacuo* and the crude residue purified by silica gel flash chromatography (isocratic: 40% Et_2O/hexane) to afford tertiary alcohols **19** (599 mg, 90%) and **S7** (37.4 mg, 5%) as white, crystalline solids.

Data for **19** (major diastereomer, peak 2): $[\alpha]_D^{25.0} = -20.5°$ (c = 0.900, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.70 (d, *J* = 2.4 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.03 (dd, *J* = 13.2, 2.7 Hz, 1H), 2.61 (dd, *J* = 13.2, 10.0 Hz, 1H), 2.08 (ddd, *J* = 11.9, 10.6, 7.9 Hz, 1H), 1.95 (ddd, *J* = 13.8, 10.4, 3.6 Hz, 1H), 1.83 (dd, *J* = 12.8, 2.6 Hz, 1H), 1.78 – 1.57 (m, 4H), 1.57 – 1.34 (m, 5H), 1.34 – 1.23 (m, 2H), 1.01 (s, 3H), 0.99 (s, 3H), 0.96 (dd, *J* = 12.9, 5.6 Hz, 2H), 0.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 158.9, 125.9, 122.8, 108.9, 98.4, 76.2, 55.9, 55.6, 51.7, 50.1, 45.4, 38.7, 38.0, 36.0, 35.0, 33.9, 33.3, 30.8, 28.5, 26.6, 26.3, 21.3, 21.0.

FTIR (NaCl, thin film) 3474 (br), 3000, 2946, 2930, 2862, 1603, 1568, 1482, 1461, 1435, 1410, 1294, 1272, 1212, 1198, 1151, 1130, 1054, 1038, 999, 937, 926, 876, 831, 756 cm.$^{-1}$

HRMS (MM) calc'd for $C_{24}H_{34}BrO_2$ $[M–OH]^+$ 433.1737, found 433.1685.

Data for **S7 (**minor diastereomer, peak 1): $[\alpha]_D^{25.0}$ = –27.7° (c = 0.950, $CHCl_3$).

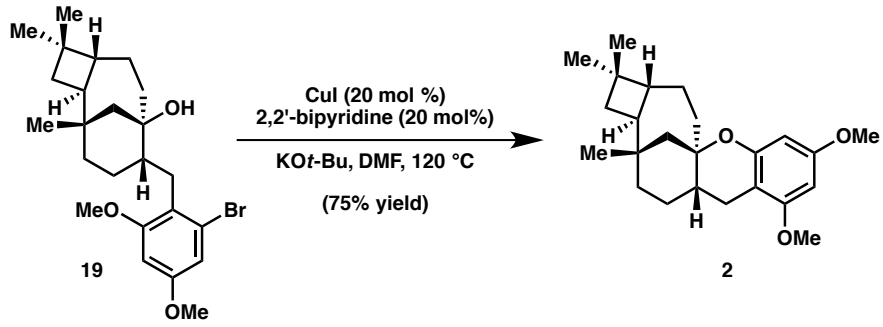
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 2.5 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.85 (dd, *J* = 13.6, 5.8 Hz, 1H), 2.59 (dd, *J* = 13.6, 8.1 Hz, 1H), 2.29 (dddd, *J* = 11.4, 8.0, 5.8, 3.5 Hz, 1H), 1.98 (ddd, *J* = 11.0, 9.4, 6.7 Hz, 2H), 1.80 – 1.52 (m, 4H), 1.52 – 1.37 (m, 4H), 1.37 – 1.26 (m, 4H), 1.25 (s, 1H), 0.94 (s, 6H), 0.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 158.5, 126.1, 123.0, 109.2, 98.3, 75.2, 55.8, 55.7, 49.3, 46.4, 45.4, 41.0, 38.5, 36.9, 36.6, 33.8, 30.5, 30.4, 29.2, 27.6, 24.2, 24.1, 21.5.

FTIR (NaCl, thin film) 3482 (br), 2998, 2945, 2928, 2859, 1690, 1648, 1602, 1567, 1482, 1459, 1435, 1409, 1381, 1364, 1294, 1273, 1211, 1198, 1154, 1134, 1051, 1039, 973, 937, 830, 809, 756.

HRMS (MM) calc'd for $C_{24}H_{35}BrO_3Na$ $[M+Na]^+$ 475.1818, found 475.1858.

Preparation of pentacycle 2.



Aryl bromide **19** (274 mg, 0.607 mmol) was added to each of two 20 mL scintillation vials and pumped inside a N_2-filled glovebox, where CuI (23.1 mg, 0.121 mmol, 0.200 equiv), 2,2'-bipyridine (18.9, 0.121 mmol, 0.200 equiv), and KO*t*-Bu (204, 1.82 mmol, 3.00 equiv) were added as solids to each. Dry DMF (6.10 mL) was then added, the reaction sealed under N_2 with a Teflon screw-cap and heated to 120 °C in a pre-heated aluminum block inside the glovebox for 3.5 hours. After cooling to room temperature, the reaction mixtures were combined and loaded directly onto a short silica gel column, pre-equilibrated with 5% Et_2O/hexane. The column was eluted with 5% Et_2O/hexane (isocratic) to afford pentacycle **2** (339 mg, 75%) as a white solid: $[\alpha]_D^{25.0}$ = +42.4° (c = 1.08, $CHCl_3$).

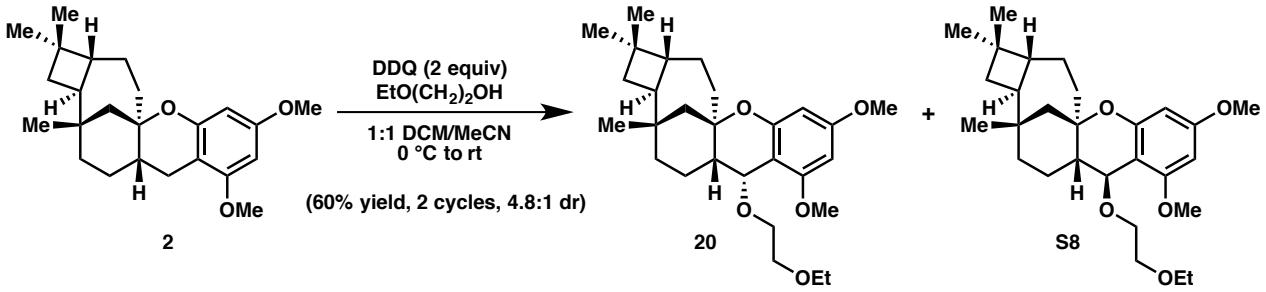
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (d, *J* = 2.4 Hz, 1H), 6.00 (d, *J* = 2.4 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 2.55 (dd, *J* = 16.6, 4.0 Hz, 1H), 2.20 – 2.03 (m, 2H), 1.97 (dd, *J* = 12.6, 2.3 Hz, 1H), 1.77 (dddd, *J* = 18.7, 9.0, 7.4, 4.8 Hz, 2H), 1.69 – 1.55 (m, 4H), 1.52 – 1.41 (m, 3H), 1.32 (t, *J* = 10.7, 9.6 Hz, 2H), 1.32 – 1.20 (m, 1H), 1.17 (dd, *J* = 12.6, 1.1 Hz, 1H), 0.99 (s, 3H), 0.97 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 158.3, 154.4, 104.5, 94.2, 90.8, 79.9, 55.5, 55.4, 48.0, 44.3, 40.9, 38.0, 36.9, 35.6, 35.1, 33.5, 30.8, 28.4, 27.1, 26.5, 22.8, 20.9, 19.9.

FTIR (NaCl, thin film) 2995, 2945, 2928, 2862, 2843, 1617, 1589, 1494, 1460, 1420, 1363, 1288, 1215, 1201, 1186, 1164, 1145, 1108, 1074, 1054, 1033, 1008, 942, 928, 810 cm.$^{-1}$

HRMS (MM) calc'd for $C_{24}H_{35}O_3$ $[M+H]^+$ 371.2581, found 371.2578.

Preparation of benzylic ethers 20 and S8.[10]



To a flame-dried 25 mL round-bottom flask was added pentacycle **2** (80.0 mg, 0.216 mmol) and the atmosphere exchanged three times for argon. A 1:1 mixture of dry MeCN/DCM (6.40 mL) was then added, followed by ethoxyethanol (1.54 mL) via syringe and the solution cooled to 0 °C. A previously prepared stock solution of DDQ in dry MeCN (0.860 mL, 0.508 M, 2.00 equiv) was then added dropwise. The reaction turned grey/blue immediately upon addition of DDQ and slowly turned green-blue by the end of addition. Once the addition was complete, the reaction was lifted from the ice bath and gradually warmed to room temperature. The color became an olive green-brown after 1 hour, indicating the reaction had stalled at ~50% conversion (as judged by TLC). At this point, the reaction was quenched with a saturated solution of aqueous $NaHCO_3$ and stirred vigorously for 10 minutes before the layers were separated. The aqueous layer was extracted twice more with DCM and the combined organic layers were washed with one portion of DI H_2O, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography: SiO_2 was first deactivated by applying a few drops of aqueous NH_4OH (28%) to the top of a dry column and equilibrating with 100 mL of 5% Et_2O/hexane. The crude residue was then applied and eluted with fresh 5% Et_2O/hexane until unreacted **2** elutes completely, then 20% Et_2O/hexane until complete elution of second diastereomer to afford a mixture of **20** and **S8** (41.0 mg, 41% yield), and recovered starting material **2** (40.8 mg, 51%). The recovered starting material was re-subjected to the reaction conditions described above to afford additional **20** and **S8** (18.8 mg, 60% total over 2 cycles) and **2** (15.2 mg, 74% overall brsm). Analytically

pure samples of **20** and **S8** were obtained by preparative TLC (30% Et_2O, 1% Et_3N/hexane) and a representative spectrum of the mixture as used in the next step is also provided.

Data for **20** (major diastereomer, peak 1): $[\alpha]_D^{25.0}$ = +43.5° (c = 0.815, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, *J* = 2.4 Hz, 1H), 5.94 (d, *J* = 2.3 Hz, 1H), 4.27 (d, *J* = 3.3 Hz, 1H), 3.98 (dt, *J* = 9.8, 4.9 Hz, 1H), 3.81 (dd, *J* = 10.9, 5.1 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.58 (dd, *J* = 5.9, 4.9 Hz, 2H), 3.53 (q, *J* = 7.0 Hz, 2H), 2.48 – 2.36 (m, 1H), 2.21 (qd, *J* = 14.4, 4.1 Hz, 1H), 2.10 (ddd, *J* = 12.2, 10.7, 7.9 Hz, 1H), 2.00 (dd, *J* = 12.7, 2.3 Hz, 1H), 1.79 – 1.61 (m, 3H), 1.59 – 1.41 (m, 4H), 1.42 – 1.20 (m, 4H), 1.20 (t, *J* = 7.0 Hz, 3H), 0.99 (s, 3H), 0.98 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 159.7, 154.7, 106.6, 93.8, 91.2, 80.5, 72.1, 71.4, 70.5, 66.7, 55.4, 55.4, 49.3, 47.6, 46.1, 39.4, 39.3, 36.3, 34.8, 33.5, 32.4, 30.8, 26.8, 23.1, 22.3, 20.8, 15.4.

FTIR (NaCl, thin film) 2948, 2930, 2864, 1614, 1589, 1491,1462, 1438, 1424, 1365, 1353, 1332, 1320, 1287, 1215, 1202, 1189, 1166, 1148, 1109, 1053, 1033, 1005, 951, 921, 866, 811, 731, 638 cm.$^{-1}$

HRMS (MM) calc'd for $C_{24}H_{33}O_3$ $[M–O(CH_2)_2OEt]^+$ 369.2424, found 369.2430.

Data for **S8** (minor diastereomer, peak 2): $[\alpha]_D^{25.0}$ = +29.6° (c = 0.230, $CHCl_3$).

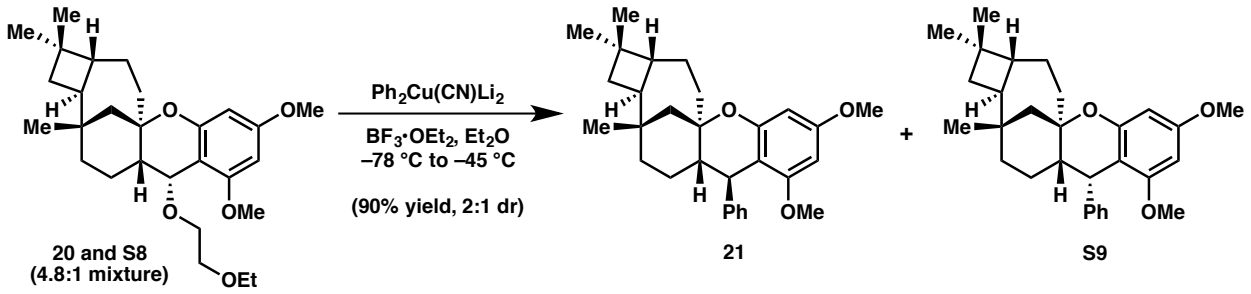
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (d, *J* = 2.4 Hz, 1H), 5.92 (d, *J* = 2.4 Hz, 1H), 4.30 (d, *J* = 10.4 Hz, 1H), 3.78 (s, 3H), 3.75 (ddd, *J* = 9.1, 3.0, 1.3 Hz, 1H), 3.73 (s, 3H), 3.58 – 3.45 (m, 5H), 2.24 – 2.04 (m, 2H), 1.92 (ddt, *J* = 14.7, 9.9, 3.2 Hz, 2H), 1.80 – 1.64 (m, 2H), 1.65 – 1.40 (m, 5H), 1.36 – 1.19 (m, 4H), 1.19 (t, *J* = 7.0 Hz, 3H), 0.97 (s, 3H), 0.96 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 160.0, 155.9, 105.8, 94.2, 91.7, 81.7, 73.4, 70.5, 67.8, 66.7, 55.5, 55.4, 48.2, 47.2, 44.4, 37.8, 37.2, 35.6, 35.1, 33.2, 30.8, 28.4, 26.4, 23.7, 20.9, 20.4, 15.4.

FTIR (NaCl, thin film) 2947, 2934, 2864, 1613, 1587, 1490, 1459, 1438, 1421, 1364, 1349, 1312, 1288, 1267, 1245, 1216, 1202, 1147, 1107, 1054, 1034, 1002, 973, 943, 868. 812, 736, 636 cm.$^{-1}$

HRMS (MM) calc'd for $C_{24}H_{33}O_3$ $[M–O(CH_2)_2OEt]^+$ 369.2424, found 369.2427.

Preparation of diarylmethanes 21 and S9.



A 10 mL round-bottom flask containing CuCN (11.9 mg, 0.133 mmol, 2.05 equiv) was flame-dried under vacuum. After cooling to room temperature, the flask was backfilled with argon and dry Et_2O (2.70 mL) was added via syringe. The suspension was cooled to –78 °C under argon and PhLi (0.140 mL, 1.9 M in dibutyl ether, 0.266 mmol, 4.09 equiv) was added dropwise. After stirring at –78 °C for 5 minutes, the reaction was warmed to 0 °C and stirred for an additional 30 minutes. The higher-order cuprate was then cooled back to –78 °C and the 4.8:1 mixture of benzylic ethers **20** and **S8** (30.0 mg, 0.065 mmol) was as a solution in Et_2O (1.00 mL). The reaction was stirred for 1-2 minutes before BF_3•OEt_2 (0.160 mL, 1.30 mmol, 20.0 equiv) was added dropwise via syringe. The reaction was stirred at –78 °C for 10 minutes, then quickly transferred to a pre-equilibrated bath at –55 °C, which was allowed to –50 °C over 5 minutes, then maintained at or just below –45 °C for another 30 minutes. The reaction was checked for completion by TLC, then quenched with aqueous $NaHCO_3$ and warmed to room temperature. The layers were separated and the aqueous layer extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (isocratic: 5% Et_2O/hexane) to afford diarylmethanes **21** and **S9** (26.3 mg, 90%) as a 2:1 inseparable mixture, white solid: $[\alpha]_D^{25.0}$ = +2.08° (c = 1.23, $CHCl_3$).

^{1}H NMR (2:1 dr, asterisk denotes minor diastereomer, 400 MHz, $CDCl_3$) δ 7.24 – 6.96 (m, 5H), 6.10* (d, *J* = 2.4 Hz, 1H), 6.07 (d, *J* = 2.5 Hz, 1H), 6.03* (d, *J* = 2.4 Hz, 1H), 5.93 (d, *J* = 2.4 Hz, 1H), 4.10* (d, *J* = 6.4 Hz, 1H), 3.79* (s, 3H), 3.76 (s, 3H), 3.46* (s, 3H), 3.47 (d, *J* = 11.3 Hz, 1H), 3.20 (s, 3H), 2.23 – 2.06 (m, 1H), 2.00 (dd, *J* = 12.7, 2.4 Hz, 1H), 1.93* (dd, *J* = 12.6, 2.5 Hz, 1H), 1.88 – 1.73 (m, 2H), 1.73 – 1.60 (m, 3H), 1.55 – 1.41 (m, 4H), 1.39 – 1.26 (m, 5H), 1.20 (q, *J* = 13.1, 12.1 Hz, 1H), 1.00 (s, 3H), 0.99 (s, 3H), 0.92* (s, 3H), 0.83 (s, 3H), 0.82* (s, 3H), 0.74* (s, 3H).

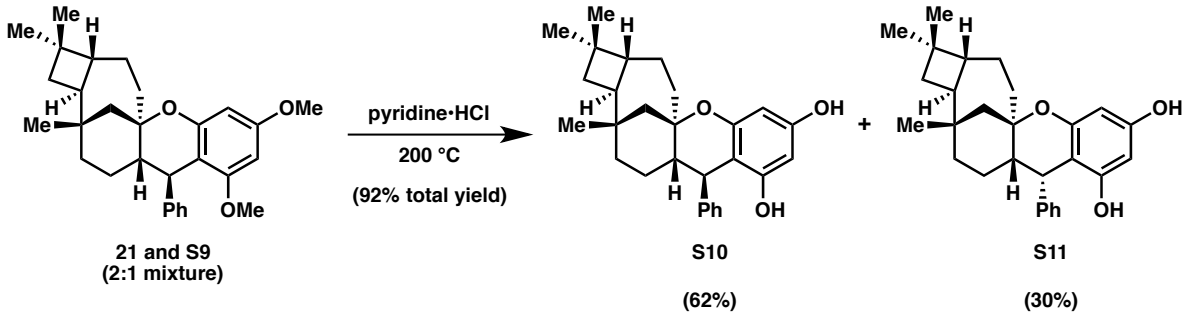
^{13}C NMR (**20**, major diastereomer, 101 MHz, $CDCl_3$) δ 160.0, 159.2, 155.2, 146.7, 129.8, 127.7, 125.4, 109.2, 94.5, 92.7, 80.4, 55.3, 55.2, 50.7, 48.1, 44.3, 41.9, 37.9, 36.9, 35.6, 35.1, 33.3, 30.8, 28.2, 26.3, 24.3, 20.9, 20.2.

^{13}C NMR (**S9**, minor diastereomer 101 MHz, $CDCl_3$) δ 160.1, 159.2, 155.1, 141.5, 128.9, 127.0, 125.5, 106.4, 94.1, 91.5, 80.7, 55.6, 55.4, 50.0, 45.8, 44.3, 39.3, 38.5, 36.7, 35.5, 35.0, 33.2, 32.7, 30.8, 26.2, 25.8, 20.9, 20.4.

FTIR (NaCl, thin film) 3081, 3059, 3025, 2998, 2948, 2934, 2864, 2843, 1614, 1588, 1490,1460, 1454, 1440, 1420, 1364, 1307, 1288, 1274, 1249, 1216, 1202, 1166, 1148, 1123, 1105, 1076, 1054, 1033, 1005, 943, 870, 811, 759, 740, 701 cm.$^{-1}$

HRMS (MM) calc'd for $C_{30}H_{39}O_3$ $[M+H]^+$ 447.2894, found 447.2905.

Preparation of resorcinols S10 and S11.



Solid pyridine•HCl (1.44 g, 12.5 mmol, 307 equiv) was weighed into each of two 2-dram vials, containing a 2:1 mixture of diarylmethanes **21** and **S9** (18.2 mg, 0.041 mmol). The vials were sealed with a Teflon screw-cap under a stream of argon and heated to 200 °C in a pre-heated aluminum block for 2.5 hours. (Note: it is important to choose a vial/heating block combination that will cover the entire volume of the solid to ensure that it stays completely melted during the course of the reaction). The reactions were cooled to room temperature, during which time the mixture solidified. The crude solids were dissolved in DI H_2O, and combined by pipetting dropwise into an Erlenmeyer flask containing a saturated solution of aqueous $NaHCO_3$. EtOAc was then added and the layers were separated. The aqueous layer was extracted three times with EtOAc and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (isocratic: 10% EtOAc, 1% AcOH/hexane) to separate catechols **S10** and **S11**. The concentrated fractions for each diastereomer (initially a pale orange oil) were each passed through another short plug of silica gel (eluting with 20% EtOAc/heaxnes) to remove residual AcOH and remaining trace impurities to afford **S10** (21.3 mg, 62%) and **S11** (10.3 mg, 30%) as white solids.

Data for **S10** (major diastereomer, peak 1): $[\alpha]_D^{25.0}$ = –28.2° (c = 0.475, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.26 (m, 5H), 6.00 (d, *J* = 2.6 Hz, 1H), 5.88 (d, *J* = 2.6 Hz, 1H), 4.73 (s, 1H), 4.46 (s, 1H), 3.49 (d, *J* = 11.4 Hz, 1H), 2.16 (ddd, *J* = 12.3, 10.4, 7.9 Hz, 1H), 2.01 (dd, *J* = 12.8, 2.3 Hz, 1H), 1.85 – 1.58 (m, 4H), 1.54 – 1.44 (m, 2H), 1.44 – 1.30 (m, 4H), 1.28 (m, 1H), 1.18 (d, *J* = 12.9 Hz, 1H), 1.10 – 1.03 (m, 1H), 1.00 (s, 3H), 0.99 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 155.8, 155.4, 142.3, 128.0, 106.3, 97.7, 96.8, 80.1, 50.5, 48.1, 44.2, 41.8, 37.8, 36.9, 35.6, 35.2, 33.3, 30.8, 28.6, 26.3, 24.0, 20.9, 20.0.

FTIR (NaCl, thin film) 3511 (br), 3386 (br), 3060, 3024, 2948, 2928, 2863, 1702, 1627, 1598, 1509, 1492, 1459, 1364, 1349, 1320, 1272, 1248, 1228, 1166, 1138, 1087, 1072, 1057, 1034, 1014, 925, 869, 831, 761, 738, 703, 667, 638, 571, 516 $cm.^{-1}$

HRMS (MM) calc'd for $C_{28}H_{35}O_3$ $[M+H]^+$ 419.2581, found 419.2591.

Data for **S11** (minor diastereomer, peak 2): $[\alpha]_D^{25.0}$ = +26.7° (c = 0.180, $CHCl_3$).

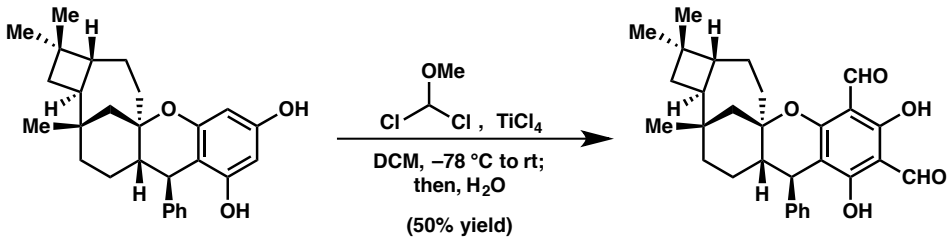
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 5H), 6.02 (d, *J* = 2.5 Hz, 1H), 5.96 (d, *J* = 2.5 Hz, 1H), 4.73 (s, 1H), 4.30 (s, 1H), 4.00 (d, *J* = 7.0 Hz, 1H), 2.16 (ddd, *J* = 12.5, 7.0, 3.9 Hz, 1H), 1.93 (dd, *J* = 12.7, 2.3 Hz, 2H), 1.79 (ddd, *J* = 12.3, 10.3, 7.8 Hz, 1H), 1.66 (ddd, *J* = 12.4, 8.7, 5.4 Hz, 1H), 1.57 – 1.43 (m, 5H), 1.39 – 1.28 (m, 4H), 1.23 – 1.12 (m, 3H), 1.09 – 0.95 (m, 2H), 0.91 (s, 3H), 0.82 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 155.7, 155.4, 138.6, 127.4, 104.8, 97.6, 95.9, 80.4, 49.7, 45.6, 44.2, 39.6, 38.3, 36.6, 35.4, 35.1, 33.2, 32.0, 30.8, 29.9, 26.1, 25.4, 20.8, 20.3.

FTIR (NaCl, thin film) 3385 (br), 3027, 2949, 2925, 2857, 1624, 1600, 1508, 1493, 1459, 1452, 1377, 1364, 1247, 1190, 1163, 1143, 1086, 1055, 1034, 1015, 925, 826, 761, 721, 701 $cm.^{-1}$

HRMS (MM) calc'd for $C_{28}H_{35}O_3$ $[M+H]^+$ 419.2581, 419.2595.

Preparation of (+)-psiguadial B (1).



S10

(+)-psiguadial B (1)
HepG2 IC_{50} = 46 nM

To a 2-dram vial was added catechol **S10** (15.4 mg, 0.037 mmol) and the atmosphere exchanged three times for N_2. DCM (1.30 mL) was then added via syringe, followed by dichloromethyl methyl ether (0.083 mL, 0.920 mmol, 25.0 equiv). The solution was cooled to –78 °C and a freshly prepared stock solution of $TiCl_4$ (0.190 mL, 0.912 M in DCM, 0.173 mmol, 4.68 equiv) was added dropwise. The reaction immediately turns dark red. The reaction was stirred at –78 °C for 5 minutes, then warmed to room temperature and stirred for an additional 3 hours and 40 minutes. DI H_2O (2.00 mL) was then added via syringe and the reaction stirred vigorously for 15 minutes before the layers were separated. The aqueous layer was extracted five times with DCM and the combined organic layers were filtered over a plug of Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (isocratic: 2% EtOAc, 1% AcOH/hexane) to afford (+)-psiguadial B (**1**) (8.7 mg, 50%) as an ivory solid. Note: **1** is streaky on SiO_2 and after an initial concentrated band elutes, approximately 12% of the product is contained in the following very dilute fractions. The natural product is weakly UV active, but can also be visualized by TLC using 2,4-dinitrophenylhydrazine stain.

$[\alpha]_D^{25.0}$ = +94.0° (c = 0.265, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.51 (s, 1H), 13.04 (s, 1H), 10.07 (s, 2H), 7.26 (dd, *J* = 14.6, 1.5 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.10 (br s, 2H), 3.49 (d, *J* = 11.5 Hz, 1H), 2.20 – 2.12 (m, 1H), 2.09 (dd, *J* = 12.7, 2.4 Hz, 1H), 1.92 (ddd, *J* = 14.9, 12.8, 4.2 Hz, 1H), 1.82 (ddd, *J* = 12.3, 8.8, 5.6 Hz, 1H), 1.73 – 1.59 (m, 3H), 1.53 – 1.44 (m, 1H), 1.49 (ddd, *J* = 11.6, 8.1, 2.9 Hz, 2H), 1.44 – 1.29 (m, 4H), 1.05 (dd, *J* = 7.6, 5.8 Hz, 1H), 1.02 (s, 3H), 1.00 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 191.5, 169.6, 168.5, 163.5, 143.4, 128.2, 126.2, 105.7, 104.6, 104.1, 84.1, 50.0, 47.4, 44.0, 40.4, 37.6, 36.9, 35.4, 35.1, 33.4, 30.6, 29.3, 26.1, 23.9, 20.7, 20.1.

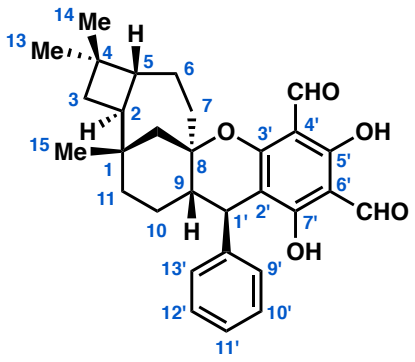
FTIR (NaCl, thin film) 3026, 2945, 2926, 2864, 2720, 1633, 1603, 1493, 1437, 1382, 1363, 1300, 1270, 1251, 1231, 1184, 1154, 1143, 1031, 1006, 976, 926, 917, 875, 851, 840, 824, 768, 701, 636, 618, 606, 564 $cm.^{-1}$

HRMS (MM) calc'd for $C_{30}H_{35}O_5$ $[M+H]^+$ 475.2479, found 475.2487.

Comparison of ^{1}H NMR spectroscopic data for natural and synthetic (+)-psigudial B (1).

carbon number	Natural (+)-psiguadial B[11] ^{1}H NMR, 500 MHz, $CDCl_3$	Synthetic (+)-psiguadial B ^{1}H NMR, 400 MHz, $CDCl_3$
5'-OH	δ 13.51 (s, 1H)	δ 13.51 (s, 1H)
7'-OH	13.04 (s, 1H)	13.04 (s, 1H)
14', 15'	10.08 (s, 2H)	10.07 (s, 2H)
9', 13'[12]	7.23 (2H)	7.26 (dd, *J* = 14.6, 1.5 Hz, 2H)
11'	7.18 (3H)	7.23 – 7.17 (m, 1H)
10', 12'	–	7.10 (br m, 2H)
1'	3.49 (d, *J* = 11.5 Hz, 1H)	3.49 (d, *J* = 11.5 Hz, 1H)
2	2.16 (1H)	2.20 – 2.12 (m, 1H)
12	2.08 (1H)	2.09 (dd, *J* = 12.7, 2.4 Hz, 1H)
7	1.93 (1H)	1.92 (ddd, *J* = 14.9, 12.8, 4.2 Hz, 1H)
5	1.82 (m, 1H)	1.82 (ddd, *J* = 12.3, 8.8, 5.6 Hz, 1H)
9	1.68 (1H)	1.73 – 1.59 (m, 3H)
6	1.65 (1H)	–
7	1.58 (m, 1H)	–
3	1.52 (1H)	1.53 – 1.44 (m, 1H)
10	1.49 (m, 2H)	1.49 (ddd, *J* = 11.6, 8.1, 2.9 Hz, 2H)
6, 11	1.41 (2H)	–
3	1.37 (1H)	1.44 – 1.29 (m, 4H)
12	1.29 (1H)	–
11	1.10 (1H)	1.05 (dd, *J* = 7.6, 5.8 Hz, 1H)
13	1.02 (s, 3H)	1.02 (s, 3H)
14	1.01 (s, 3H)	1.00 (s, 3H)
15	0.86 (s, 3H)	0.85 (s, 3H)

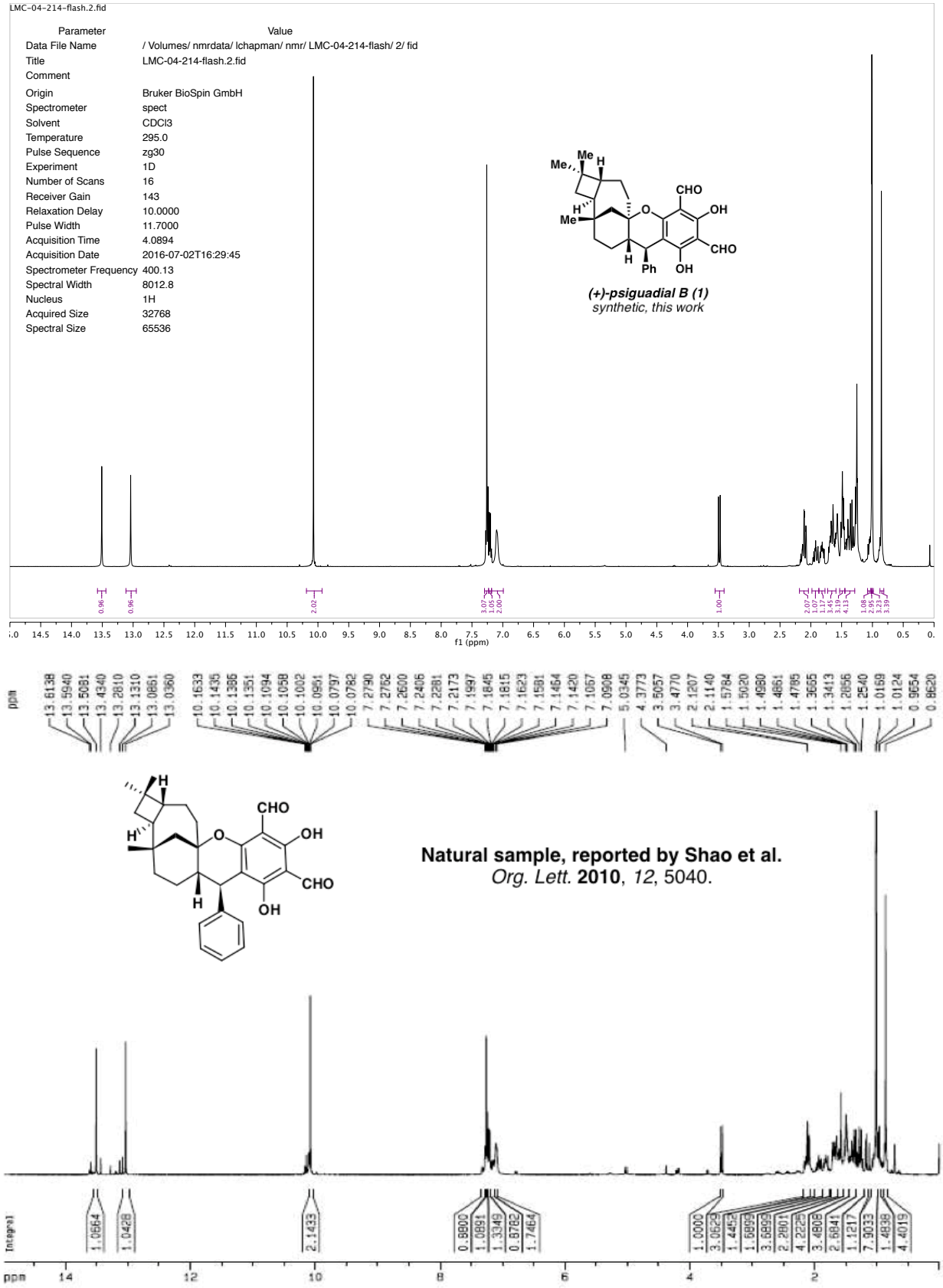
(+)-psiguadial B (**1**) carbon numbering as reported by Shao et al.[11]



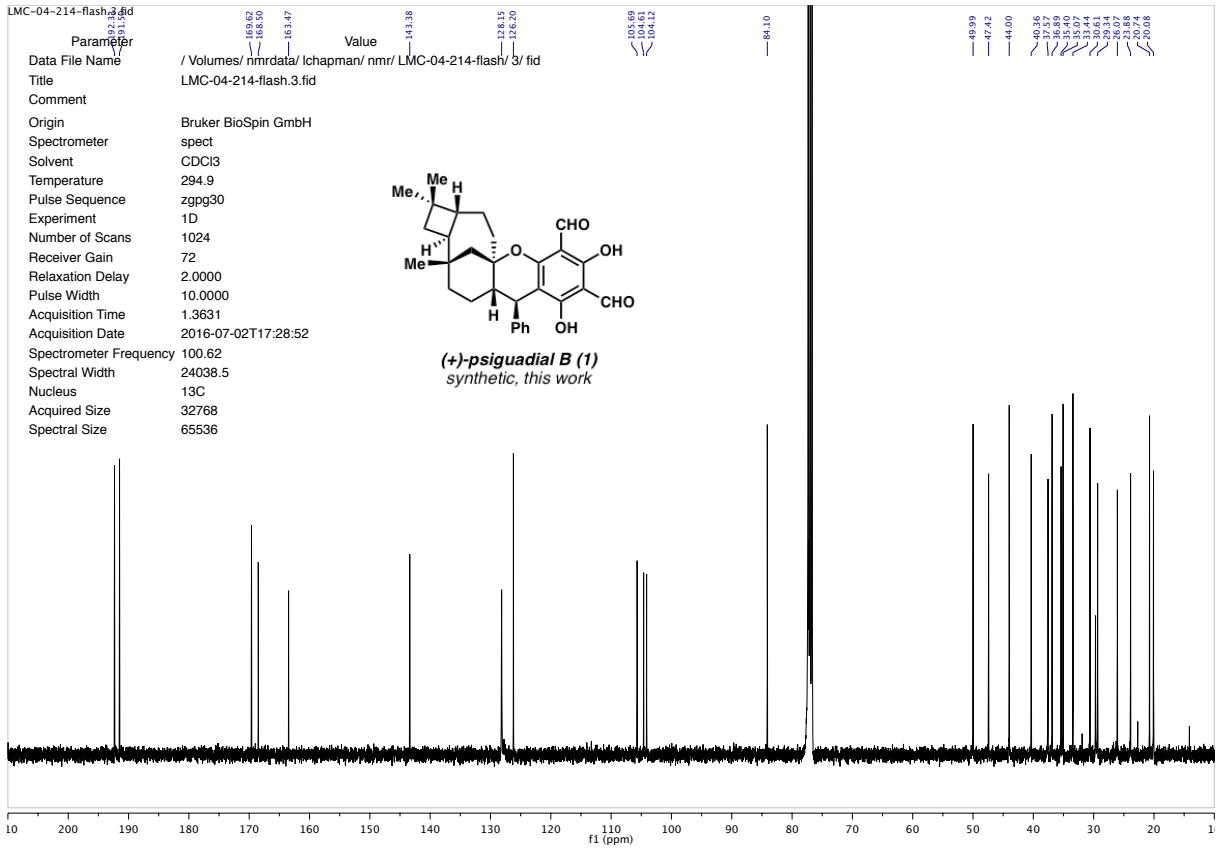
Comparison of ^{13}C NMR spectroscopic data for natural and synthetic (+)-psigudial B (1).

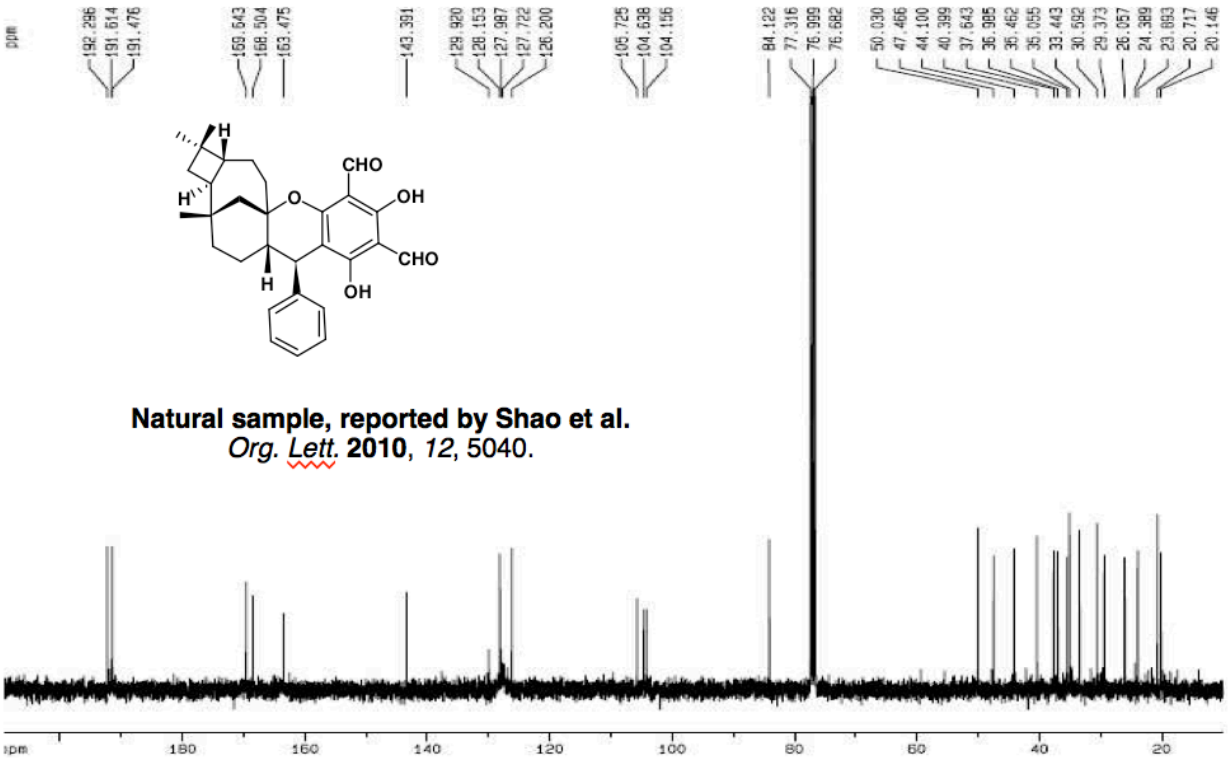
carbon number	**Natural (+)-psiguadial B**[11] ^{13}C NMR, 125 MHz, $CDCl_3$	**Synthetic (+)-psiguadial B**[13] ^{13}C NMR, 101 MHz, $CDCl_3$	Δ
15'	192.3	192.3	0.0
14'	191.4	191.5	0.1
7'	169.6	169.6	0.0
5'	168.5	168.5	0.0
3'	163.5	163.5	0.0
8'	143.4	143.4	0.0
9', 11', 13’	128.2	128.2	0.0
10', 12'	126.2	126.2	0.0
2'	105.7	105.7	0.0
4'	104.6	104.6	0.0
6'	104.2	104.1	-0.1
8	84.1	84.1	0.0
9	50.0	50.0	0.0
12	47.5	47.4	-0.1
5	44.1	44.0	-0.1
1'	40.4	40.4	0.0
11	37.6	37.6	0.0
2	37.0	36.9	-0.1
3	35.5	35.4	-0.1
4	35.1	35.1	0.0
1	33.4	33.4	0.0
13	30.6	30.6	0.0
7	29.4	29.3	-0.1
15	26.1	26.1	0.0
10	23.9	23.9	0.0
14	20.7	20.7	0.0
6	20.1	20.1	0.0

^{1}H NMR spectral comparison of natural and synthetic (+)-psigudial B (1).



^{13}C NMR spectral comparison of natural and synthetic (+)-psigudial B (1).





X-Ray crystallographic data for 11.

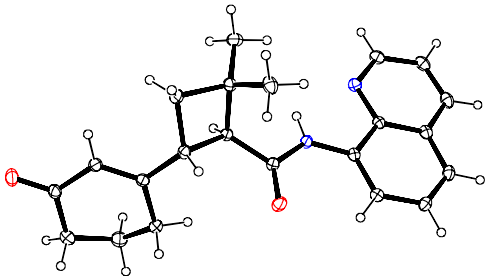


Table 1. Crystal data and structure refinement for crystal01.

Identification code	Crystal01	
Empirical formula	$C_{22}H_{24}N_2O_2$	
Formula weight	348.43	
Temperature	119.98 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.3942(5) Å	α = 90°.
	b = 11.6678(9) Å	β = 90 °.
	c = 24.848(2) Å	γ = 90 °.
Volume	1853.8(3) $Å^3$	
Z	4	
Density (calculated)	1.248 Mg/m^3	
Absorption coefficient	0.636 mm^{-1}	
F(000)	744	
Crystal size	0.237 x 0.093 x 0.082 mm^3	
Theta range for data collection	3.557 to 71.792°.	
Index ranges	-7<=h<=7, -14<=k<=14, -28<=l<=30	
Reflections collected	41642	
Independent reflections	3620 [R(int) = 0.0313]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9883 and 0.8875	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3620 / 0 / 237	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0782	

R indices (all data)	R1 = 0.0294, wR2 = 0.0785
Absolute structure parameter	-0.04(4)
Largest diff. peak and hole	0.255 and -0.181 e/Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for crystal01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-4024(2)	4325(1)	3741(1)	30(1)
O(2)	5981(2)	5004(1)	2361(1)	34(1)
N(1)	-3297(2)	4719(1)	4622(1)	22(1)
N(2)	-3330(2)	4949(1)	5683(1)	23(1)
C(1)	-2893(2)	4755(1)	4081(1)	21(1)
C(2)	-944(2)	5426(1)	3950(1)	19(1)
C(3)	-1002(3)	6755(1)	4055(1)	24(1)
C(4)	-3194(3)	7259(2)	3999(1)	31(1)
C(5)	36(3)	7135(2)	4574(1)	33(1)
C(6)	286(3)	6893(1)	3529(1)	26(1)
C(7)	-388(3)	5674(1)	3354(1)	22(1)
C(8)	1149(3)	4904(1)	3080(1)	22(1)
C(9)	2914(3)	5310(1)	2858(1)	23(1)
C(10)	4426(3)	4596(2)	2574(1)	26(1)
C(11)	3943(3)	3338(2)	2530(1)	38(1)
C(12)	2522(3)	2898(2)	2970(1)	40(1)
C(13)	612(3)	3648(2)	3047(1)	30(1)
C(14)	-5080(2)	4317(1)	4886(1)	20(1)
C(15)	-6783(3)	3820(1)	4640(1)	22(1)
C(16)	-8492(3)	3441(1)	4955(1)	24(1)
C(17)	-8509(3)	3560(1)	5503(1)	27(1)
C(18)	-6795(3)	4077(1)	5768(1)	24(1)
C(19)	-5062(2)	4456(1)	5460(1)	20(1)
C(20)	-3303(3)	5073(2)	6212(1)	27(1)
C(21)	-4952(3)	4734(2)	6553(1)	29(1)
C(22)	-6681(3)	4240(2)	6333(1)	29(1)

Table 3. Bond lengths [Å] and angles [°] for crystal01.

O(1)-C(1)	1.219(2)
O(2)-C(10)	1.224(2)
N(1)-C(1)	1.369(2)
N(1)-C(14)	1.397(2)
N(2)-C(19)	1.365(2)
N(2)-C(20)	1.320(2)
C(1)-C(2)	1.507(2)
C(2)-C(3)	1.574(2)
C(3)-C(4)	1.526(2)
C(3)-C(6)	1.554(2)
C(5)-C(3)	1.516(2)
C(7)-C(2)	1.551(2)
C(7)-C(6)	1.549(2)
C(7)-C(8)	1.495(2)
C(8)-C(13)	1.508(2)
C(8)-C(9)	1.342(2)
C(10)-C(11)	1.504(3)
C(10)-C(9)	1.459(2)
C(11)-C(12)	1.511(3)
C(13)-C(12)	1.515(3)
C(14)-C(15)	1.377(2)
C(14)-C(19)	1.436(2)
C(15)-C(16)	1.414(2)
C(17)-C(16)	1.369(2)
C(18)-C(17)	1.415(2)
C(18)-C(19)	1.417(2)
C(18)-C(22)	1.417(2)
C(20)-C(21)	1.410(3)
C(21)-C(22)	1.362(3)

O(1)-C(1)-C(2)	123.68(14)
O(1)-C(1)-N(1)	123.69(14)
O(2)-C(10)-C(11)	121.04(16)
O(2)-C(10)-C(9)	121.70(16)
N(1)-C(1)-C(2)	112.58(13)

N(1)-C(14)-C(19)	115.04(14)
N(2)-C(19)-C(14)	117.20(14)
N(2)-C(19)-C(18)	123.12(14)
N(2)-C(20)-C(21)	123.85(16)
C(1)-C(2)-C(3)	117.15(13)
C(1)-C(2)-C(7)	119.57(13)
C(1)-N(1)-C(14)	128.75(13)
C(4)-C(3)-C(2)	112.66(14)
C(4)-C(3)-C(6)	111.66(14)
C(5)-C(3)-C(2)	114.81(13)
C(5)-C(3)-C(4)	111.60(14)
C(5)-C(3)-C(6)	116.97(15)
C(6)-C(3)-C(2)	87.09(11)
C(6)-C(7)-C(2)	88.10(12)
C(7)-C(2)-C(3)	88.86(11)
C(7)-C(6)-C(3)	89.69(12)
C(7)-C(8)-C(13)	117.31(14)
C(8)-C(13)-C(12)	112.61(15)
C(8)-C(7)-C(2)	118.23(13)
C(8)-C(7)-C(6)	119.83(14)
C(8)-C(9)-C(10)	123.62(15)
C(9)-C(10)-C(11)	117.19(15)
C(9)-C(8)-C(13)	120.87(15)
C(9)-C(8)-C(7)	121.80(15)
C(10)-C(11)-C(12)	113.71(15)
C(11)-C(12)-C(13)	112.36(17)
C(14)-C(15)-C(16)	119.81(14)
C(15)-C(14)-C(19)	119.65(14)
C(15)-C(14)-N(1)	125.31(14)
C(16)-C(17)-C(18)	120.05(16)
C(17)-C(16)-C(15)	121.66(16)
C(17)-C(18)-C(19)	119.14(14)
C(17)-C(18)-C(22)	123.96(16)
C(18)-C(19)-C(14)	119.67(14)
C(20)-N(2)-C(19)	117.41(15)
C(21)-C(22)-C(18)	119.72(16)
C(22)-C(18)-C(19)	116.89(15)

C(22)-C(21)-C(20)	119.00(15)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal01. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	28(1)	43(1)	19(1)	1(1)	-2(1)	-12(1)
O(2)	28(1)	46(1)	27(1)	0(1)	8(1)	-4(1)
N(1)	20(1)	28(1)	18(1)	0(1)	0(1)	-4(1)
N(2)	24(1)	25(1)	21(1)	1(1)	-1(1)	1(1)
C(1)	20(1)	22(1)	20(1)	2(1)	-1(1)	0(1)
C(2)	19(1)	22(1)	17(1)	1(1)	-1(1)	-1(1)
C(3)	26(1)	23(1)	23(1)	0(1)	4(1)	-2(1)
C(4)	34(1)	28(1)	32(1)	4(1)	7(1)	8(1)
C(5)	38(1)	31(1)	29(1)	-6(1)	2(1)	-8(1)
C(6)	29(1)	23(1)	27(1)	2(1)	5(1)	-2(1)
C(7)	22(1)	26(1)	18(1)	4(1)	0(1)	-2(1)
C(8)	22(1)	26(1)	16(1)	-1(1)	-2(1)	-2(1)
C(9)	26(1)	25(1)	19(1)	1(1)	0(1)	-4(1)
C(10)	24(1)	37(1)	16(1)	-1(1)	0(1)	-3(1)
C(11)	36(1)	39(1)	40(1)	-16(1)	10(1)	-3(1)
C(12)	45(1)	27(1)	48(1)	-8(1)	12(1)	-4(1)
C(13)	31(1)	28(1)	32(1)	-6(1)	8(1)	-8(1)
C(14)	21(1)	18(1)	21(1)	3(1)	1(1)	3(1)
C(15)	24(1)	20(1)	21(1)	2(1)	-1(1)	2(1)
C(16)	21(1)	22(1)	31(1)	3(1)	0(1)	-1(1)
C(17)	24(1)	26(1)	31(1)	5(1)	7(1)	-1(1)
C(18)	26(1)	20(1)	24(1)	3(1)	3(1)	4(1)
C(19)	22(1)	17(1)	21(1)	2(1)	0(1)	3(1)
C(20)	32(1)	28(1)	22(1)	-1(1)	-3(1)	2(1)
C(21)	38(1)	30(1)	20(1)	1(1)	2(1)	6(1)
C(22)	34(1)	28(1)	25(1)	4(1)	8(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal01.

	x	y	z	U(eq)
H(1)	-2298	4985	4831	26
H(2)	286	5078	4137	23
H(4A)	-3840	6972	3667	47
H(4B)	-3104	8096	3983	47
H(4C)	-4046	7031	4309	47
H(5A)	-803	6878	4881	49
H(5B)	144	7973	4579	49
H(5C)	1438	6799	4597	49
H(6A)	-237	7508	3290	31
H(6B)	1809	6972	3590	31
H(7)	-1698	5721	3135	26
H(9)	3195	6107	2889	28
H(11A)	5272	2902	2541	46
H(11B)	3277	3190	2177	46
H(12A)	3314	2863	3312	48
H(12B)	2067	2110	2880	48
H(13A)	-363	3523	2743	36
H(13B)	-114	3417	3382	36
H(15)	-6811	3732	4260	26
H(16)	-9656	3096	4781	29
H(17)	-9674	3295	5705	32
H(20)	-2101	5411	6371	33
H(21)	-4858	4849	6930	35
H(22)	-7806	4005	6557	35

References

1. Still, W. C., Kahn, M. & Mitra, A. *J. Org. Chem*. **1978**, *43*, 2923.
2. Prepared according to: Ghosh, A.; Banerjee, U. K.; Venkateswaran, R. V. *Tetrahedron* **1990**, *46* (8), 3077, using *p*-4-acetamidobenzenesulfonyl azide (*p*-ABSA) instead of tosyl azide. In our hands, the formylation of 2,2-dimethylcyclopentanone at the reported concentration (1.5 M) reacts rapidly upon warming to room temperature (caution: extremely exothermic on large scale!). We found that more concentrated reaction mixtures (2.2 M) react readily at 0 °C, providing for a safer protocol.
3. Reaction time varies with the age of the lamp. A UV-opaque film slowly develops on the inside surface of the flask facing the lamp upon prolonged irradiation. This film can be removed by soaking the flask in an alkali base bath (KOH, 4:1 *i*-PrOH/H_2O).
4. Prepared according to: Piers, E.; Grierson, J. R.; Lau, C. K.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 210.
5. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.
6. Sheldrick, G. M. *Acta Cryst. A* **2008**, *64*, 112.
7. See procedure on page S11.
8. Prepared according to the ligand protocol described in: Bao, H.; Qi, X.; Tambar, U. K. *J. Am. Chem. Soc.* **2011**, *133* (5), 1206. We found that the use of DCM as a reaction solvent provided higher and more reproducible yields, compared with THF.
9. Prepared according to: Wong, N. C.W.; Tucker, J. E.L.; Hansen, H. C.; Chiacchia, F. S.; McCaffrey, D. Compounds for the Prevention and Treatment of Cardiovascular Diseases. U.S. patent 188467 A1, August, 7, **2008**.
10. Extensive optimization aimed at increasing conversion of this reaction resulted in either significant decomposition, a variety of over-oxidation products, or trapping by 2,3-dichloro-5,6-dicyanohydroquinone. As a result, we found that the most efficient material throughput was achieved by running the reaction to ~50% conversion using the above protocol, and resubjecting the recovered starting material to the reaction conditions.
11. Isolation of psiguadials A and B: Shao, M.; Wang, Y.; Liu, Z.; Zhang, D.-M.; Cao, H.-H.; Jiang, R.-W.; Fan, C.-L.; Zhang, X.-Q.; Chen, H.-R.; Yao, X.-S.; Ye, W.-C. *Org. Lett.* **2010**, *12*, 5040. Except where designated, multiplicities are not specified.
12. Shao et al. report the two protons at 7.23 ppm as corresponding to the carbon signal at 126.2 ppm (carbons 10' and 12'). This is assumed to be a typographical error based on the reported plot of their HSQC spectrum and our own data showing a correlation between the proton signal at 7.26 ppm and the more downfield carbon shift at 128.2 ppm, which corresponds to carbons 9' and 13'. The remaining three aromatic proton signals are adjusted accordingly in the comparison list.
13. Center peak of $CDCl_3$ is referenced to 76.999 ppm, as shown in the Shao et al. report, see ^{13}C spectral comparison on page S31.

Enantioselective Total Synthesis of (+)-Psiguadial B

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Pasadena, California 91125
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Supporting Information 2 (Spectral Data)

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Receiver Gain	197
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-09T16:38:44
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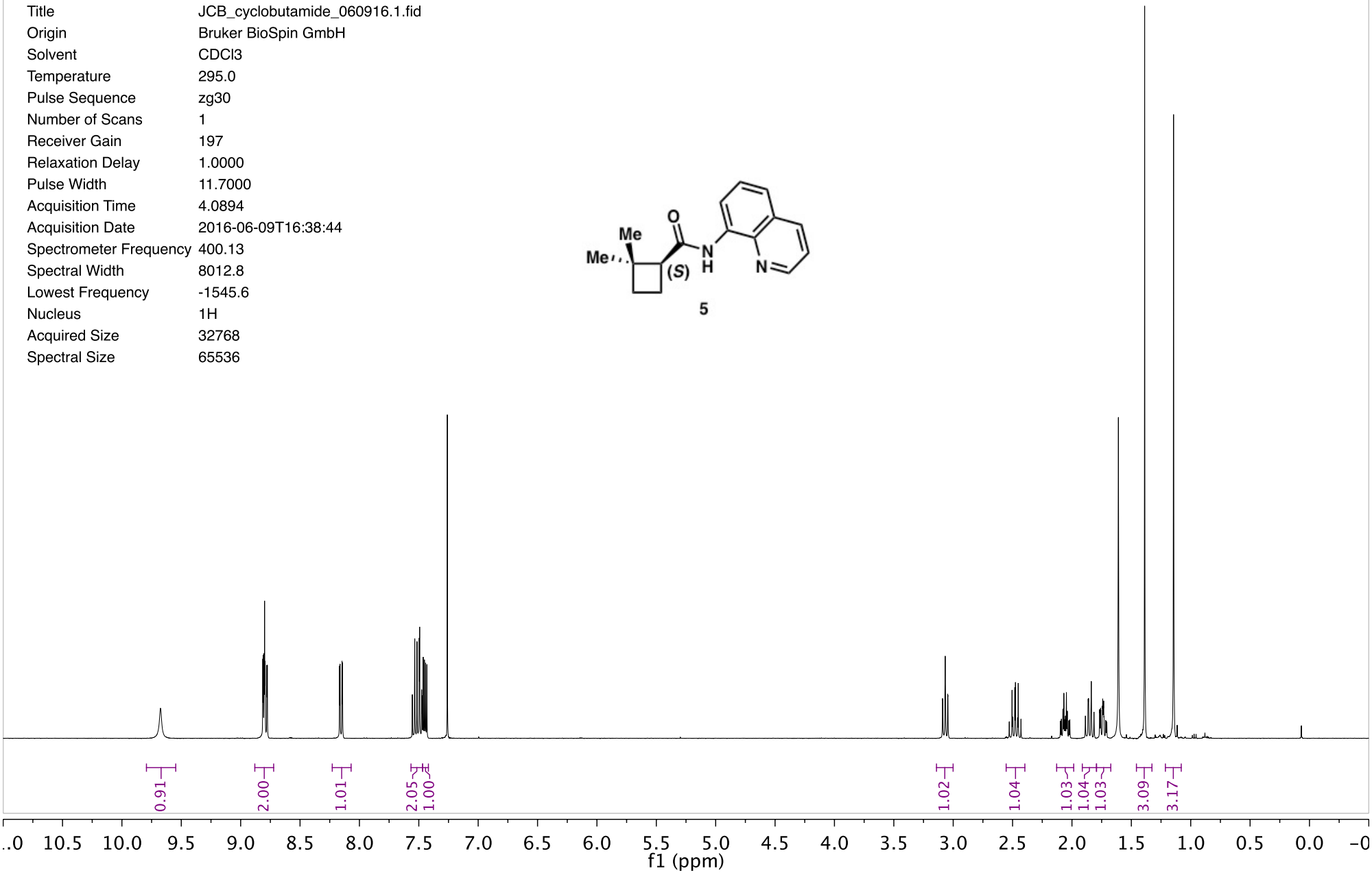
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

5



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Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-09T17:10:30
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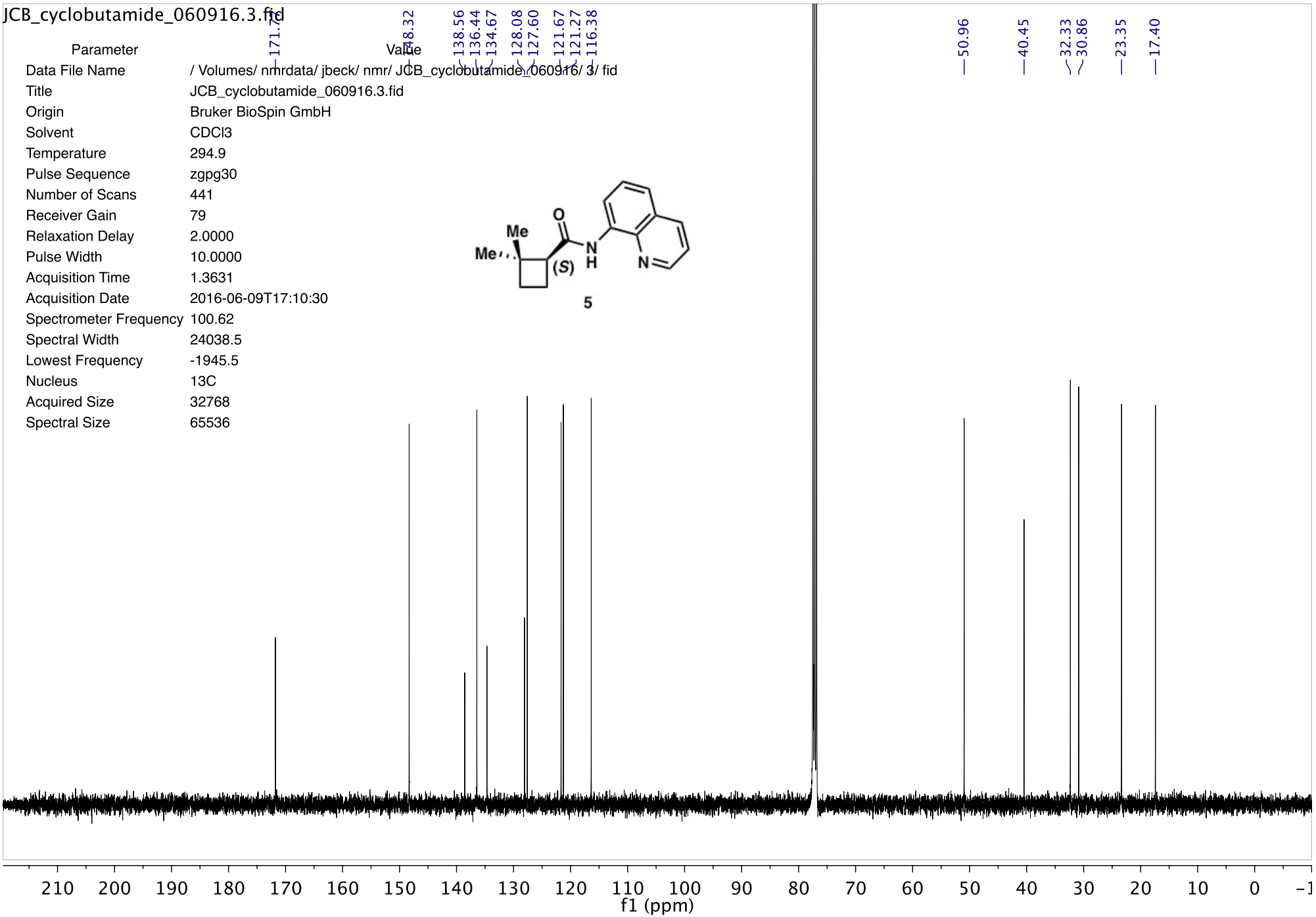
Spectral Width	24038.5
Lowest Frequency	-1945.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

5



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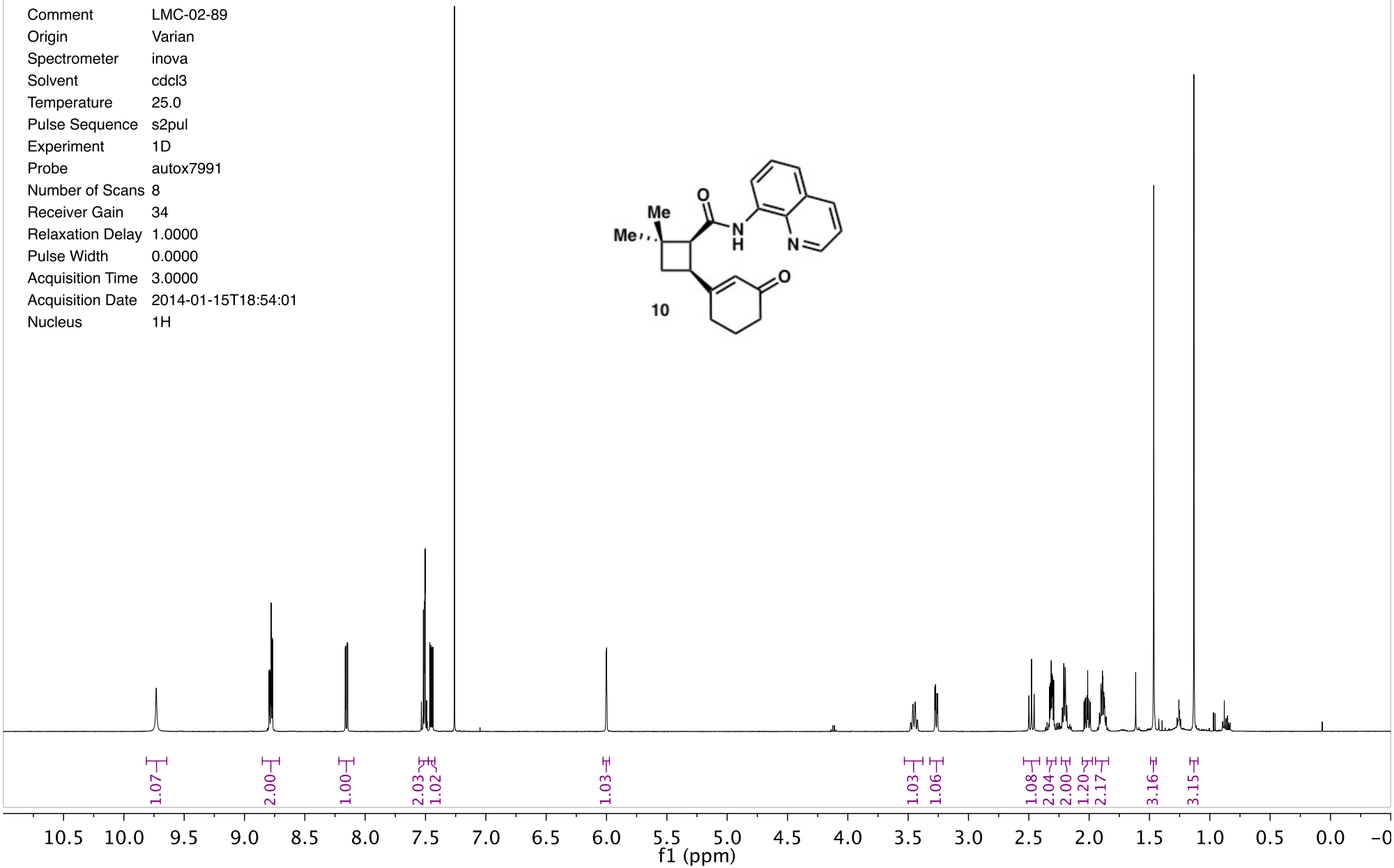
Spectrometer	inova
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	autox7991
Number of Scans	8
Receiver Gain	34
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	3.0000
Acquisition Date	2014-01-15T18:54:01
Nucleus	1H



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LMC-02-89

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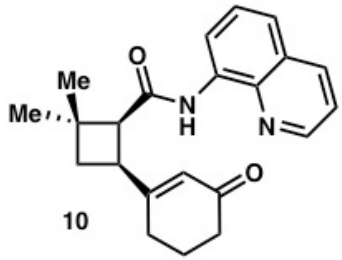
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	autox7991
Number of Scans	1000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.0420
Acquisition Date	2014-01-15T18:54:49
Nucleus	13C

199.52 170.19 166.51 148.27 138.37 136.34 134.36 127.94 127.39 124.92 121.65 121.53 116.49 56.90 37.53 37.50 36.83 35.74 29.94 27.83 24.92 22.59



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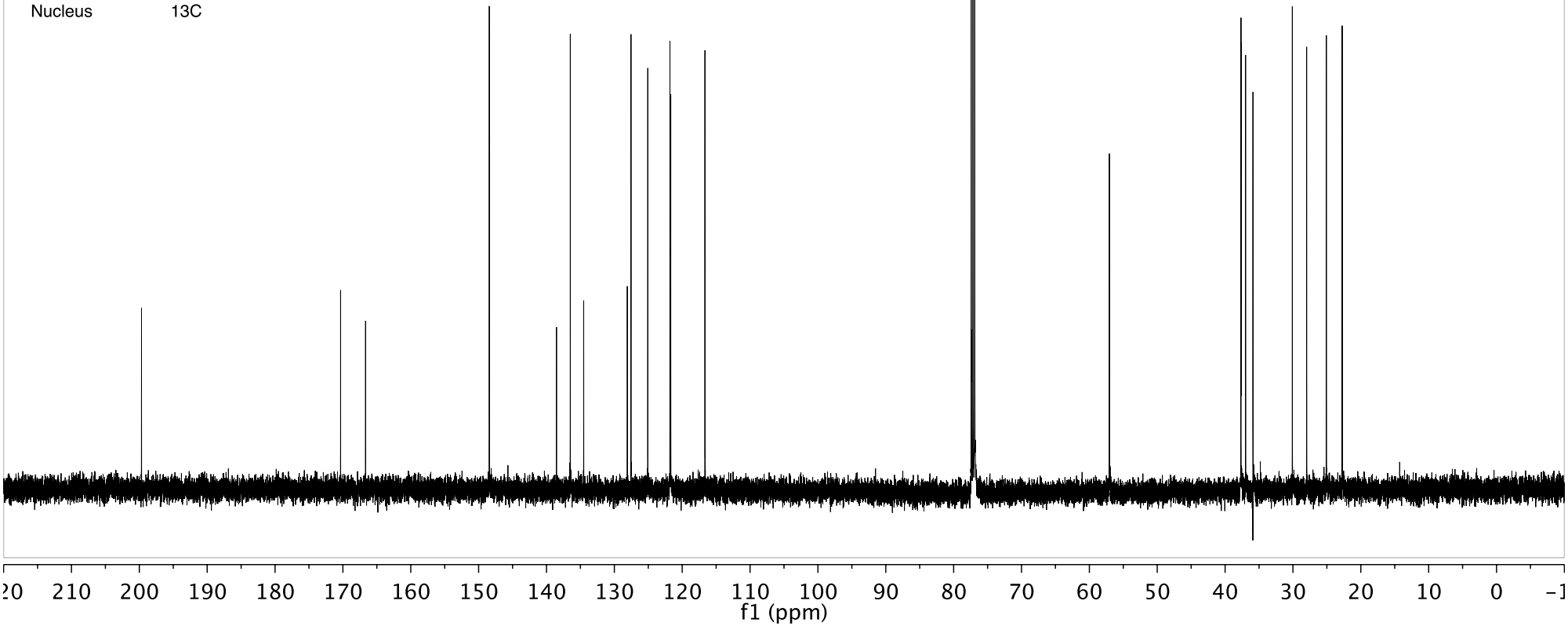

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f1 (ppm)

PROTON01
LMC-02-93trans

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Origin	Varian
Spectrometer	inova
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	autox7991
Number of Scans	8
Receiver Gain	22
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	3.0000
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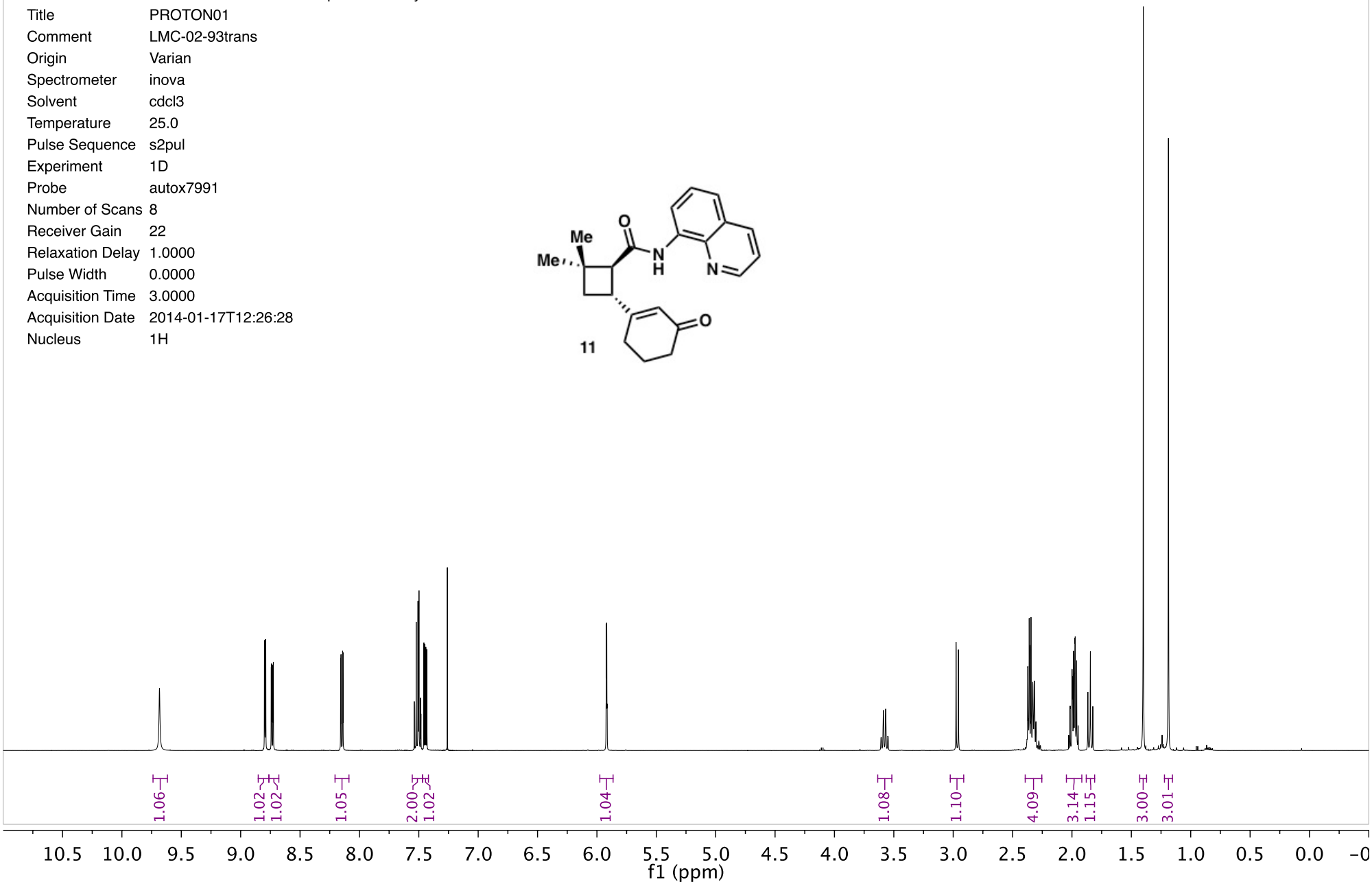
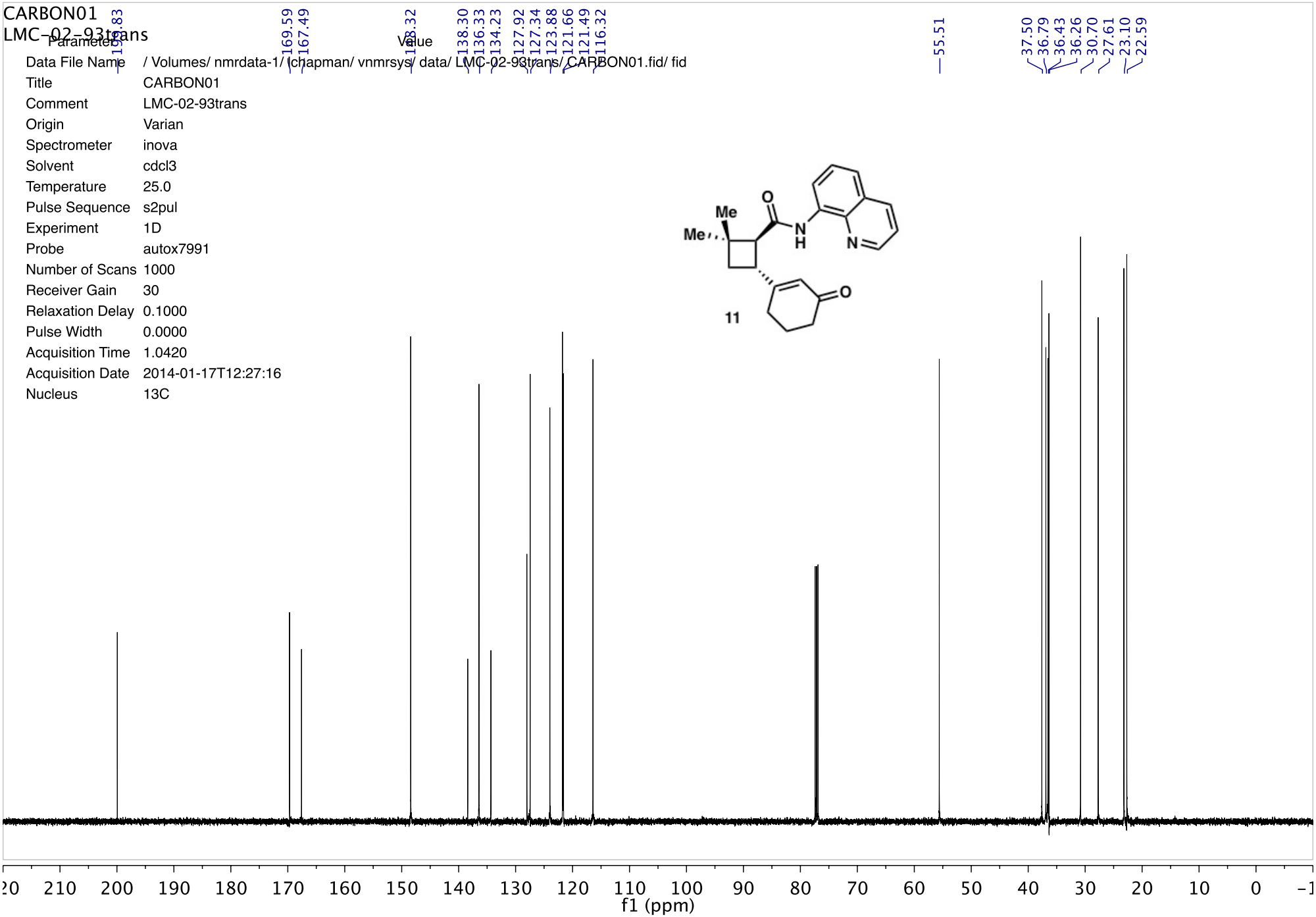
Nucleus	1H

11

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LMC-02-93trans
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Comment LMC-02-93trans
Origin Varian
Spectrometer inova
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe autox7991
Number of Scans 1000
Receiver Gain 30
Relaxation Delay 0.1000
Pulse Width 0.0000
Acquisition Time 1.0420
Acquisition Date 2014-01-17T12:27:16
Nucleus 13C
199.83
169.59
167.49
148.32
138.30
136.33
134.23
127.92
127.34
123.88
121.66
121.49
116.32
55.51
37.50
36.79
36.43
36.26
30.70
27.61
23.10
22.59
Me
Me
O
N
H
N
O
11
f1 (ppm)

LMC-04-128-spiroP1.1.fid

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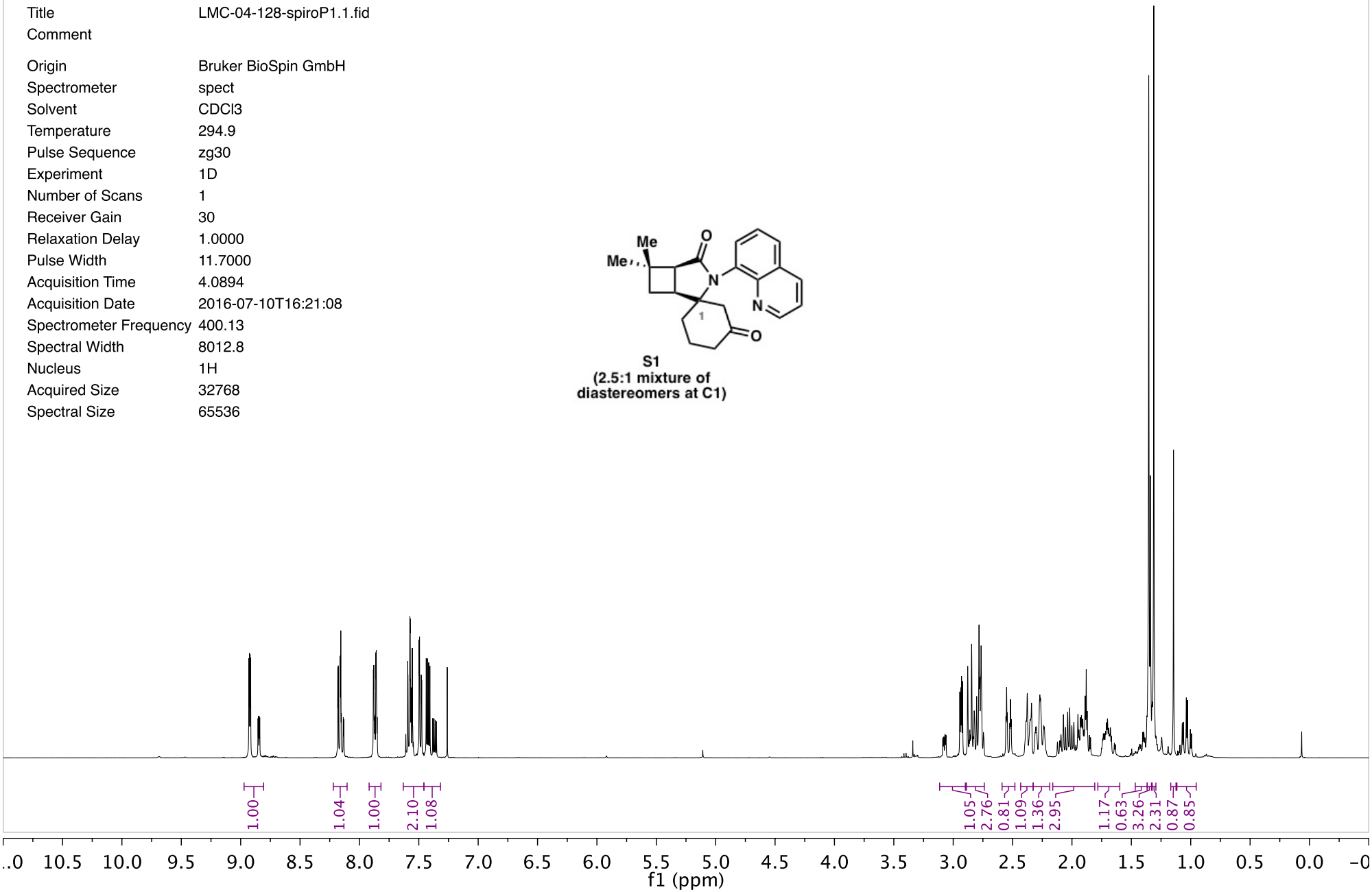
Spectrometer	spect
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-07-10T16:21:08
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

S1
(2.5:1 mixture of diastereomers at C1)



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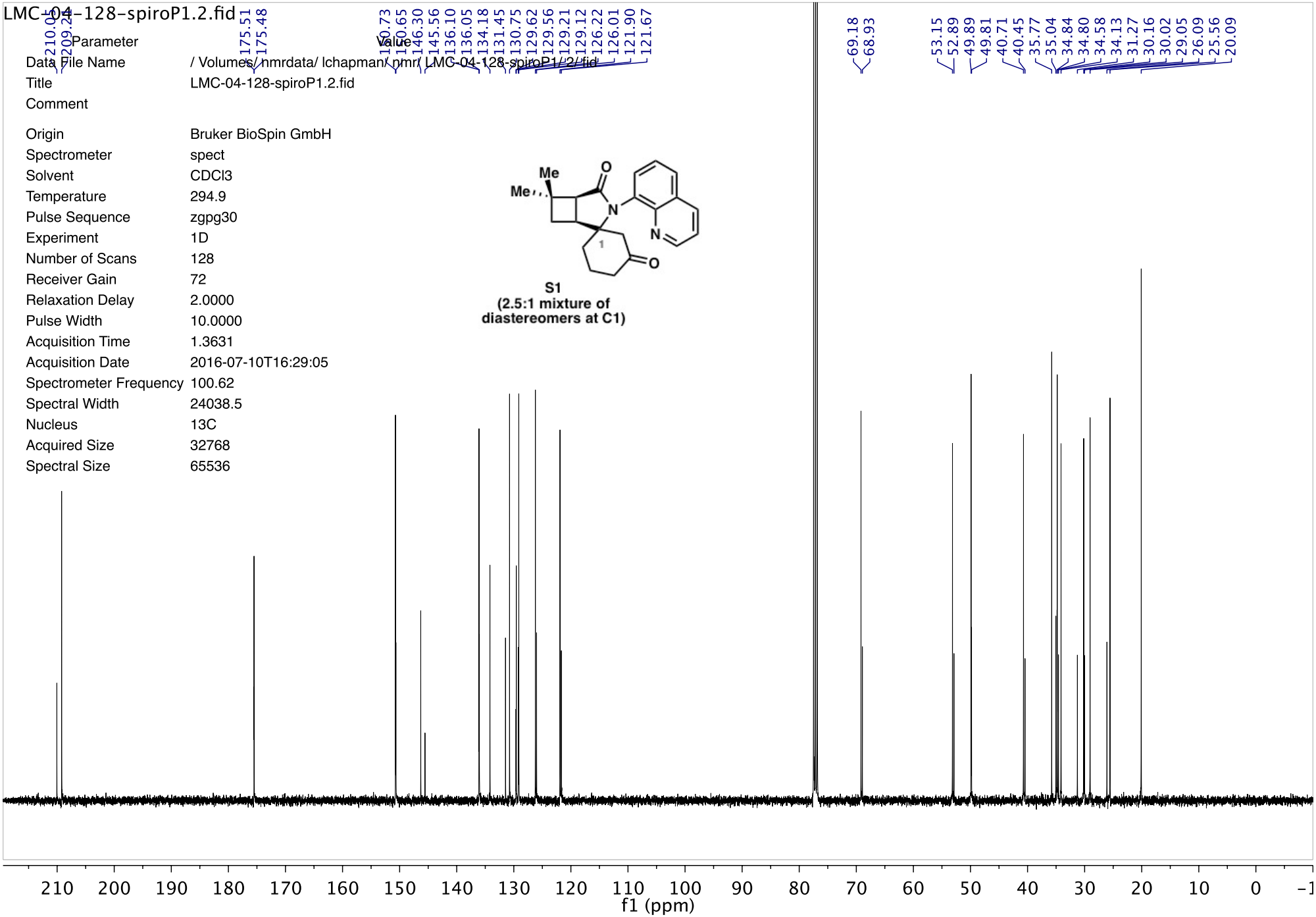
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	128
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-07-10T16:29:05
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

S1
(2.5:1 mixture of diastereomers at C1)

210.04 209.24 175.51 175.48 150.73 150.65 146.30 145.56 136.10 136.05 134.18 131.45 130.75 129.62 129.56 129.21 129.12 126.22 126.01 121.90 121.67 69.18 68.93 53.15 52.89 49.89 49.81 40.71 40.45 35.77 35.04 34.84 34.80 34.58 34.13 31.27 30.16 30.02 29.05 26.09 25.56 20.09



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Receiver Gain	30
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Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-03-10T14:57:25
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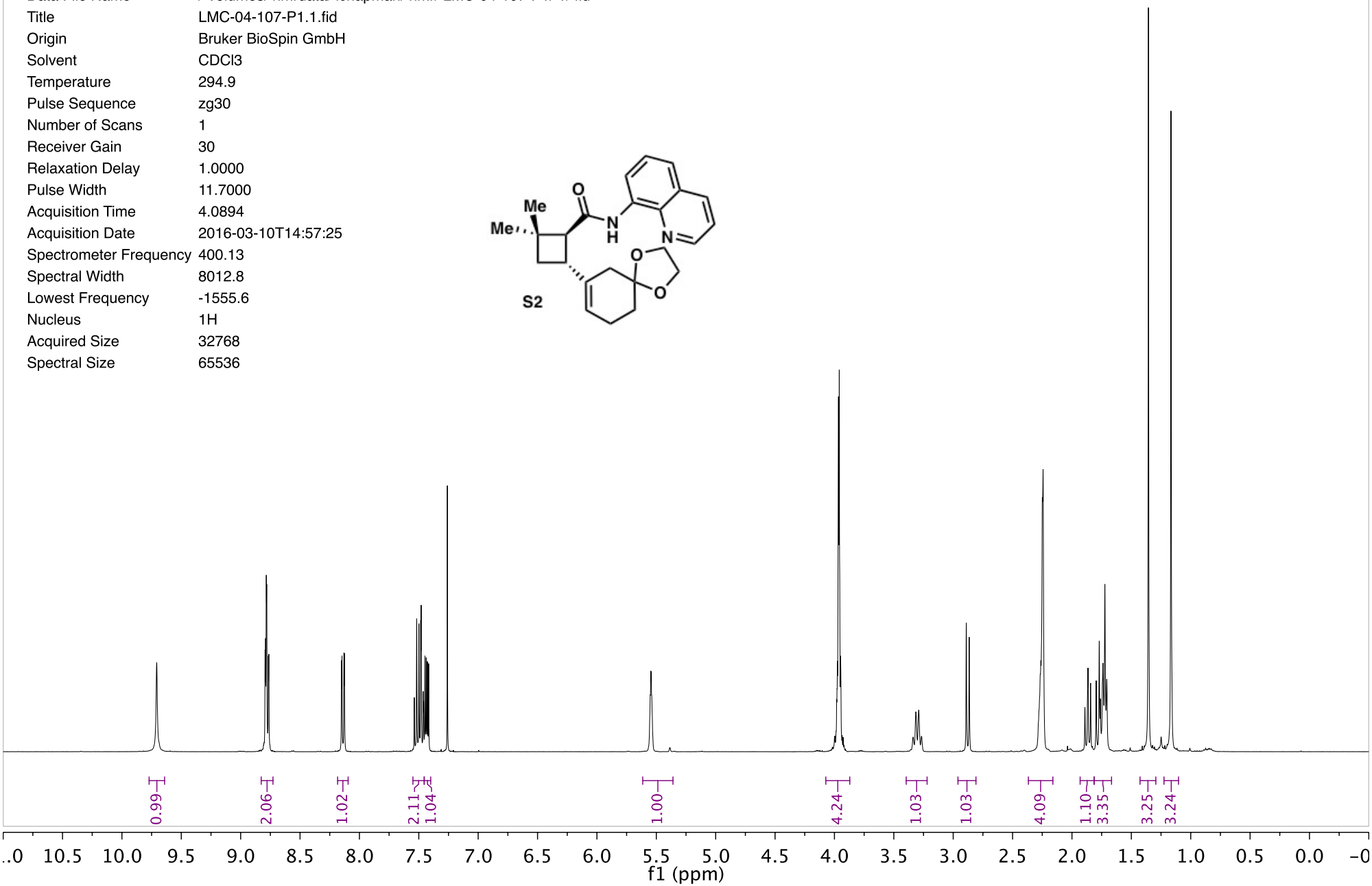
Spectral Width	8012.8
Lowest Frequency	-1555.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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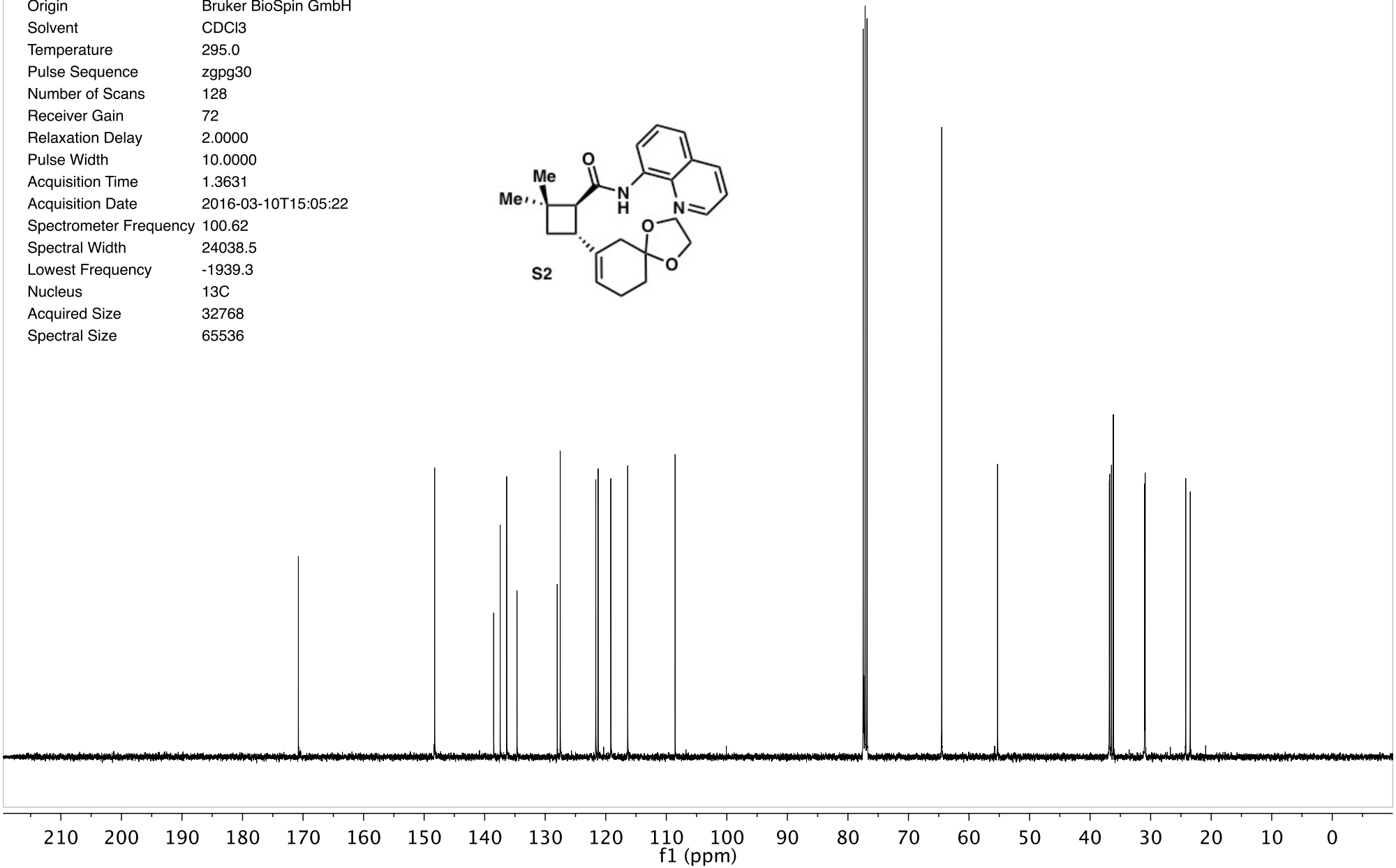
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-03-10T15:05:22
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1939.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

170.68 148.17 138.42 137.35 136.27 134.57 127.93 127.43 121.55 121.17 119.07 116.28 108.45 64.41 55.18 36.72 36.67 36.38 36.07 30.88 30.80 24.10 23.36



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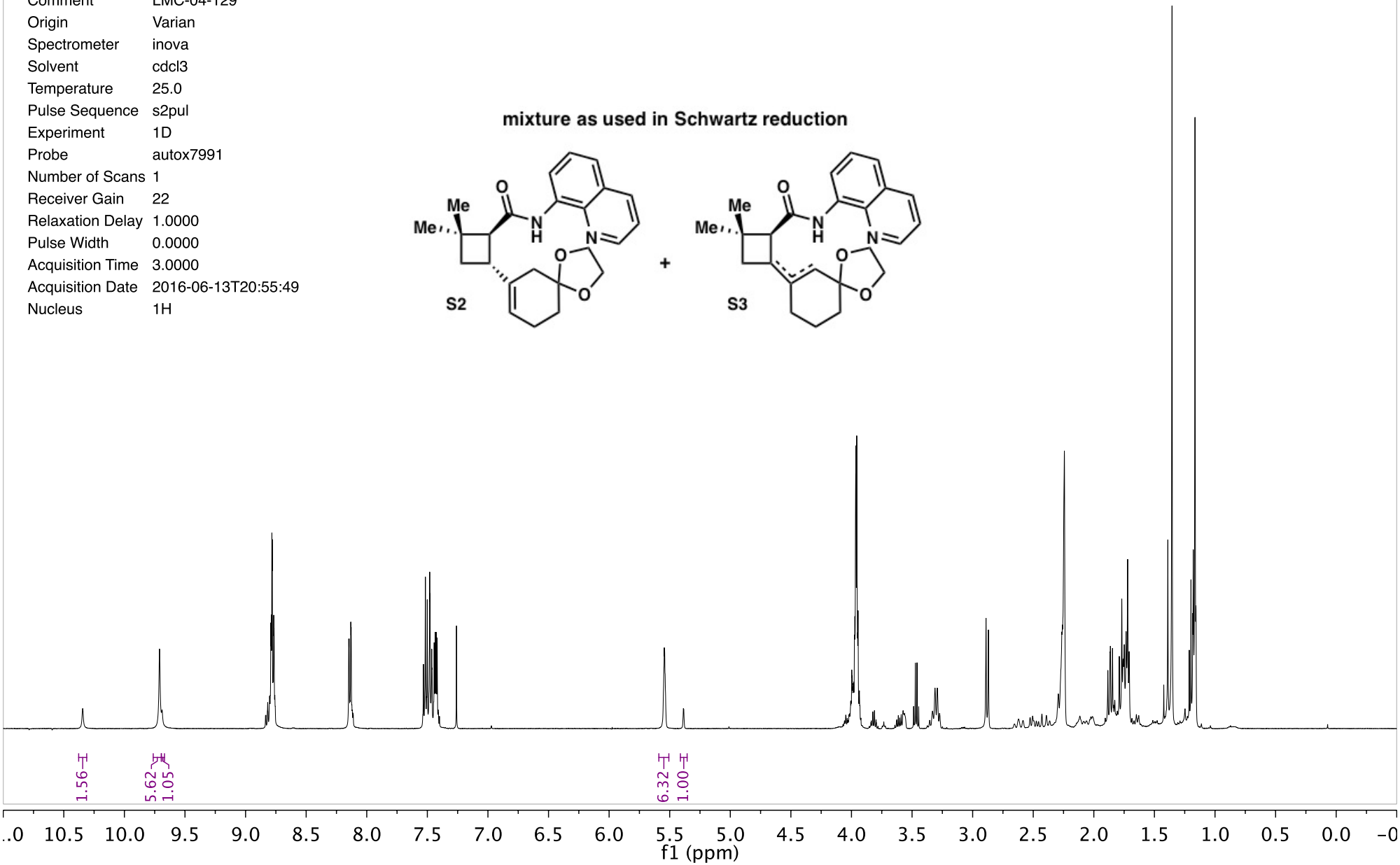
Spectrometer	inova
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	autox7991
Number of Scans	1
Receiver Gain	22
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	3.0000
Acquisition Date	2016-06-13T20:55:49
Nucleus	1H

mixture as used in Schwartz reduction



CARBON01

LMC-04-129-C13

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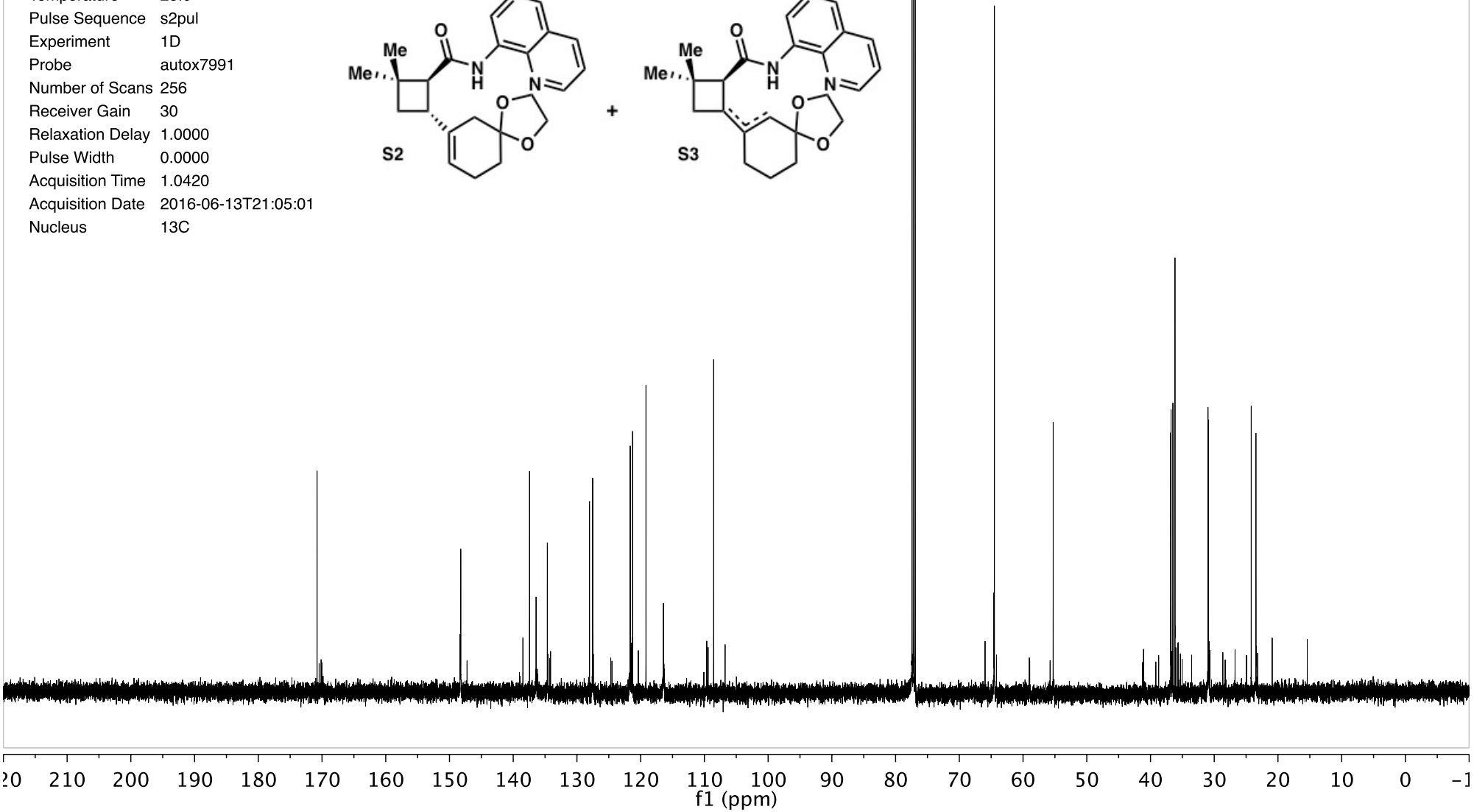
Comment	LMC-04-129-C13
Origin	Varian
Spectrometer	inova
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	autox7991
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.0420
Acquisition Date	2016-06-13T21:05:01
Nucleus	13C

170.78 170.45 170.14 170.05 148.34 148.23 147.24 138.48 137.43 136.41 134.65 134.54 134.28 134.14 128.03 127.53 127.51 127.43 124.69 124.50 121.67 121.64 121.47 121.31 121.27 120.37 119.17 116.43 109.63 109.42 108.54 106.75

65.96 64.56 64.49 64.16 59.01 58.95 55.75 55.27 41.09 36.83 36.77 36.61 36.48 36.16 36.01 35.64 35.31 30.98 30.90 30.79 30.68 28.65 26.73 24.20 23.45 23.18 20.90

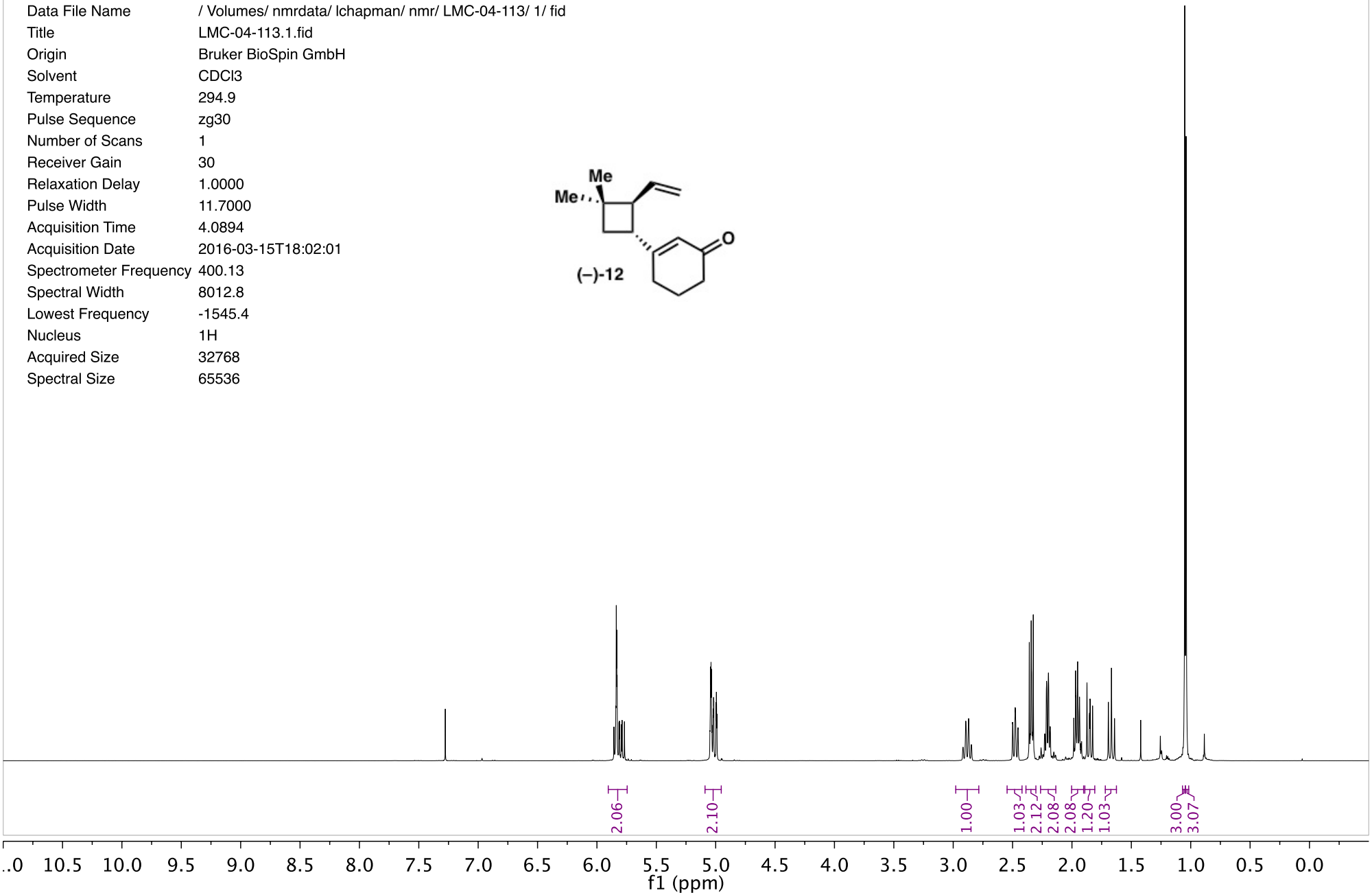
mixture as used in Schwartz reduction



LMC-04-113.1.fid

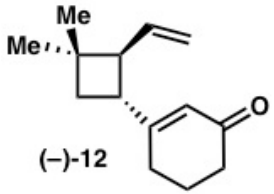
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-113/ 1/ fid
Title	LMC-04-113.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-03-15T18:02:01
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

(–)-12



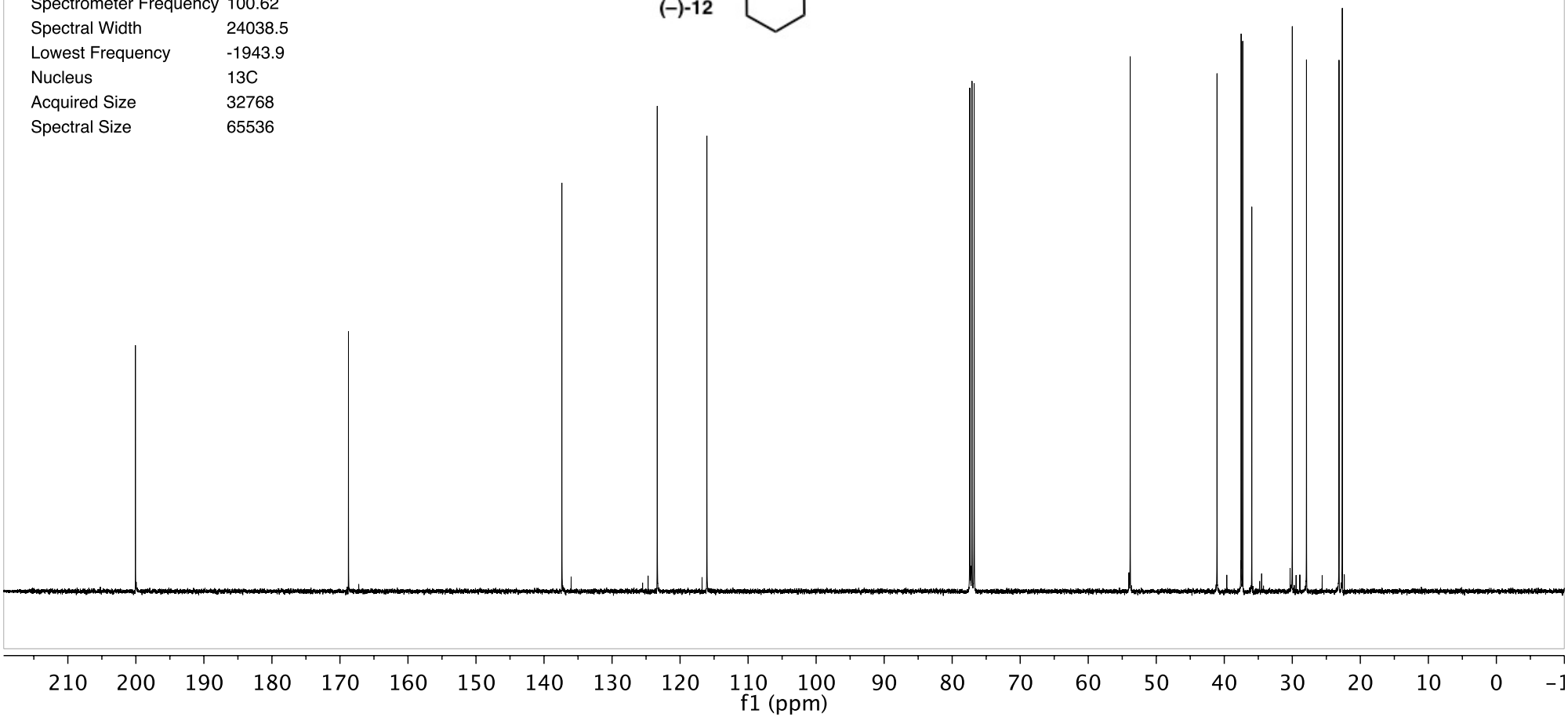
LMC-04-113.2.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-113/ 2/ fid
Title	LMC-04-113.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	79
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-03-15T18:10:33
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1943.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



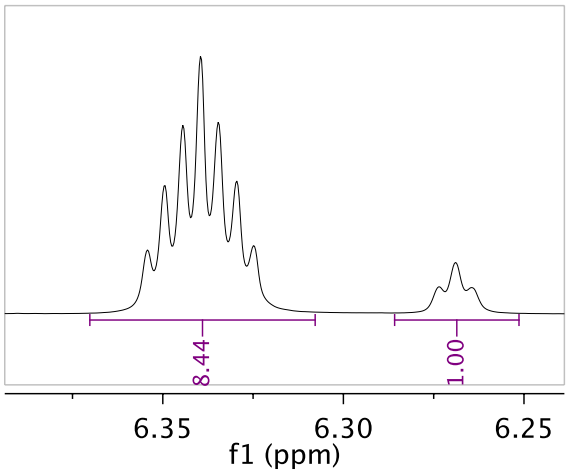
(–)-12

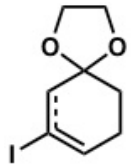
200.00
168.75
137.38
123.36
116.06
53.83
41.06
37.52
37.28
35.95
30.00
27.91
23.13
22.65



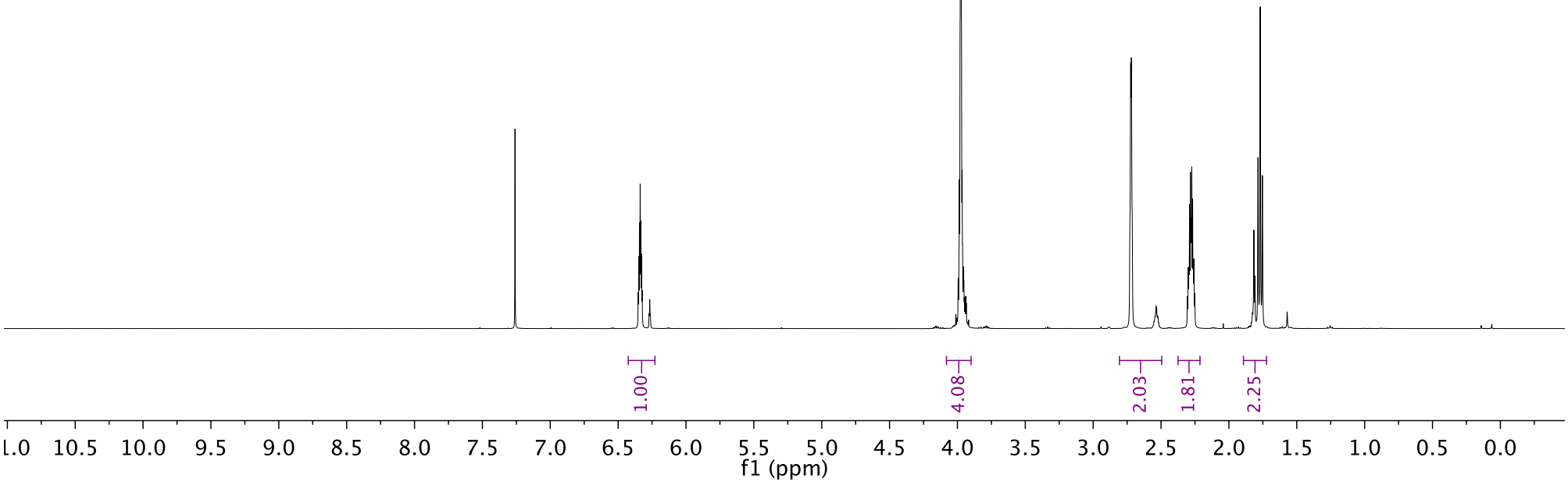
JCB_02_117_P1.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata-2/ jbeck/ nmr/ JCB_02_117_P1/ 1/ fid
Title	JCB_02_117_P1.1.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	127
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-04-01T13:22:19
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536





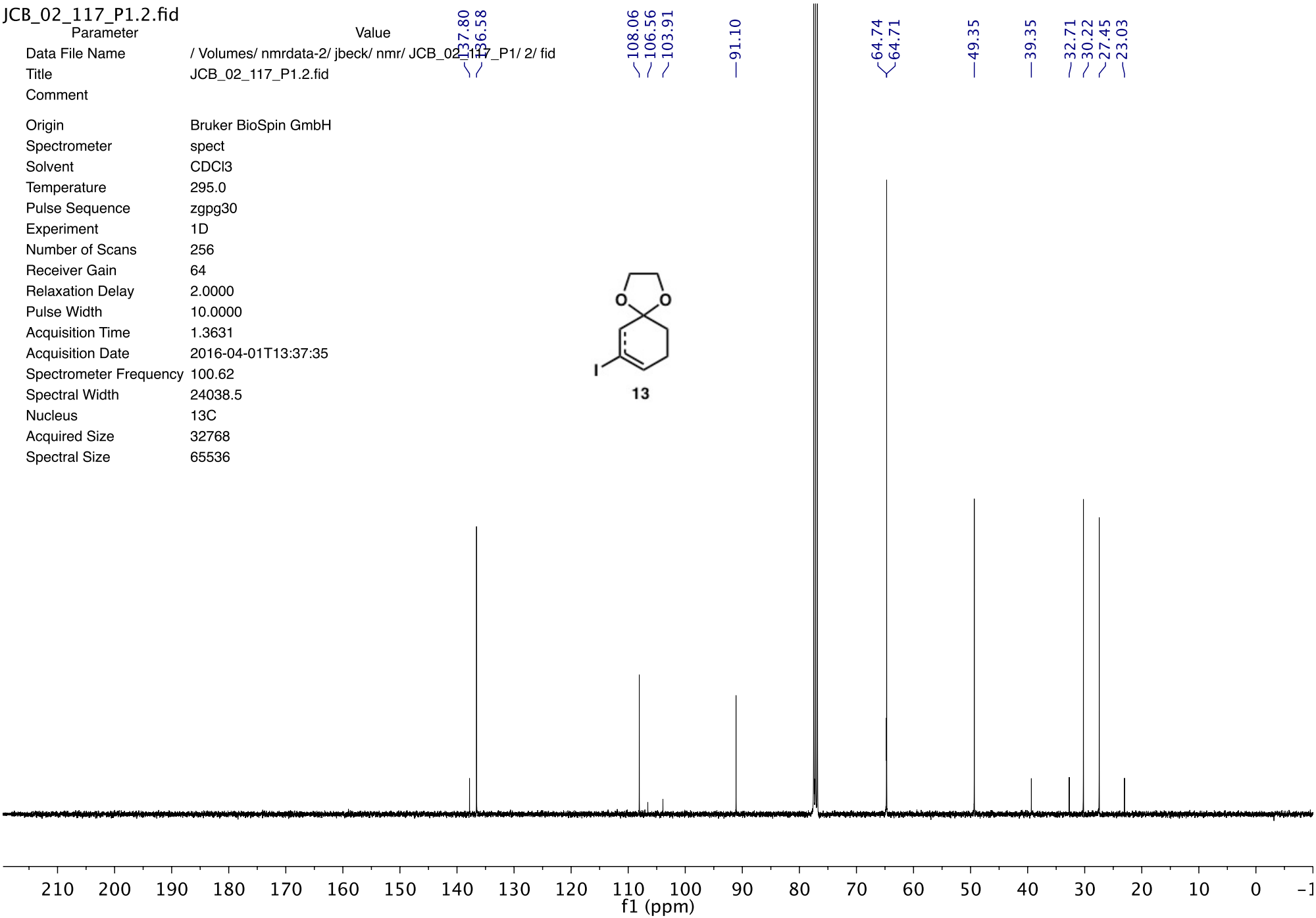
13



JCB_02_117_P1.2.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata-2/ jbeck/ nmr/ JCB_02_117_P1/ 2/ fid
Title	JCB_02_117_P1.2.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	64
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-04-01T13:37:35
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

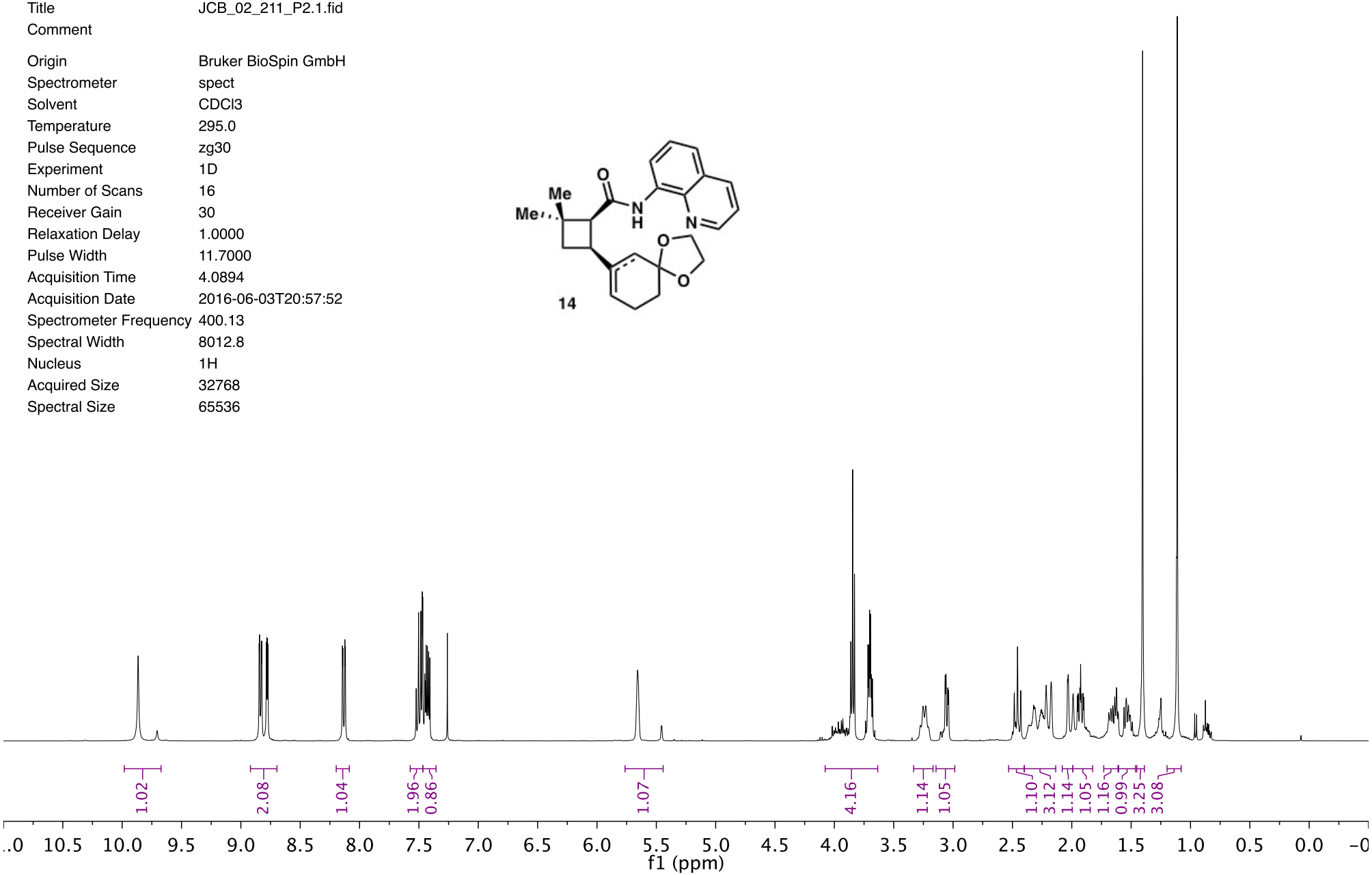
13



JCB_02_211_P2.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ jbeck/ nmr/ JCB_02_211_P2/ 1/ fid
Title	JCB_02_211_P2.1.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-03T20:57:52
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

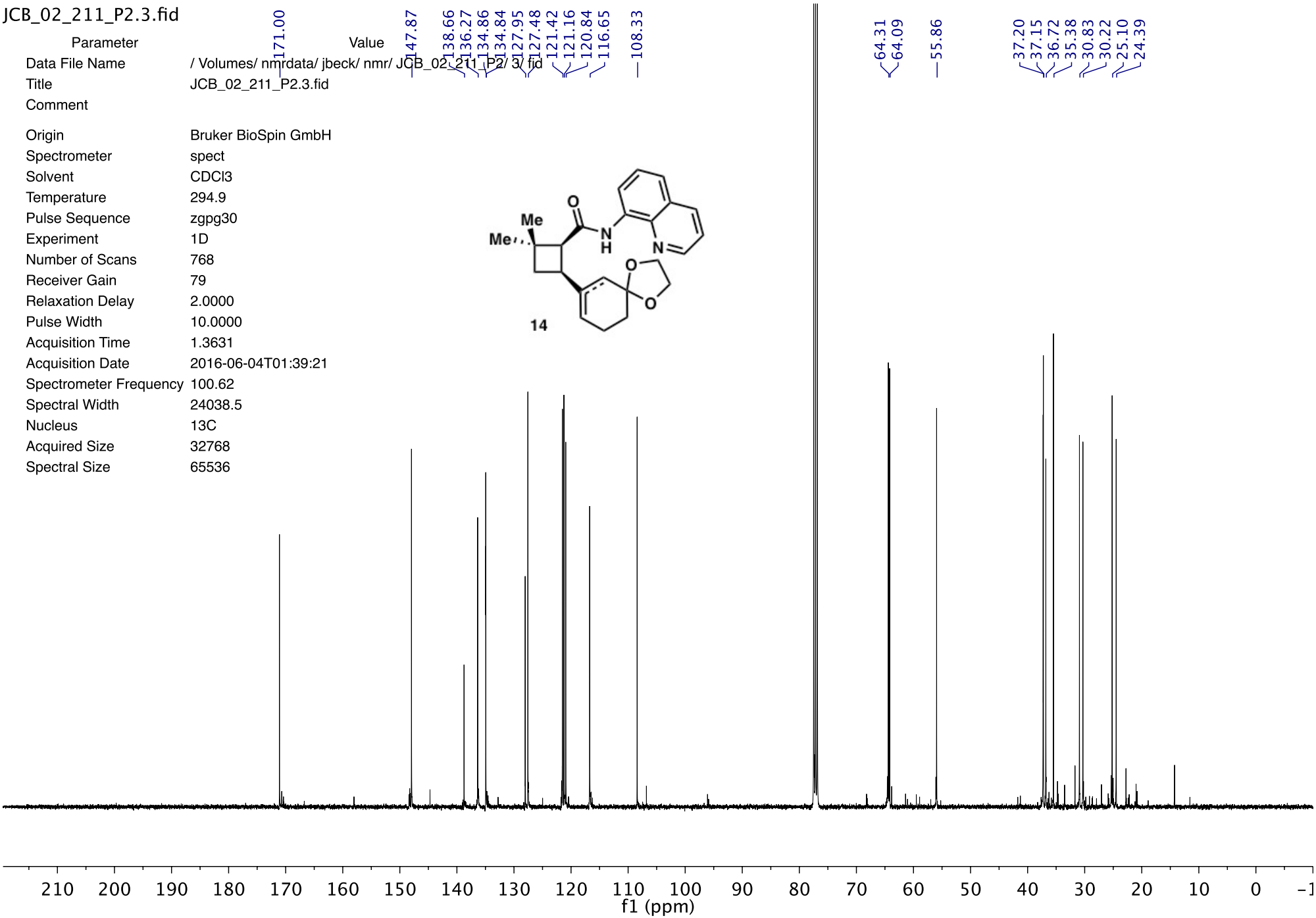
14



JCB_02_211_P2.3.fid

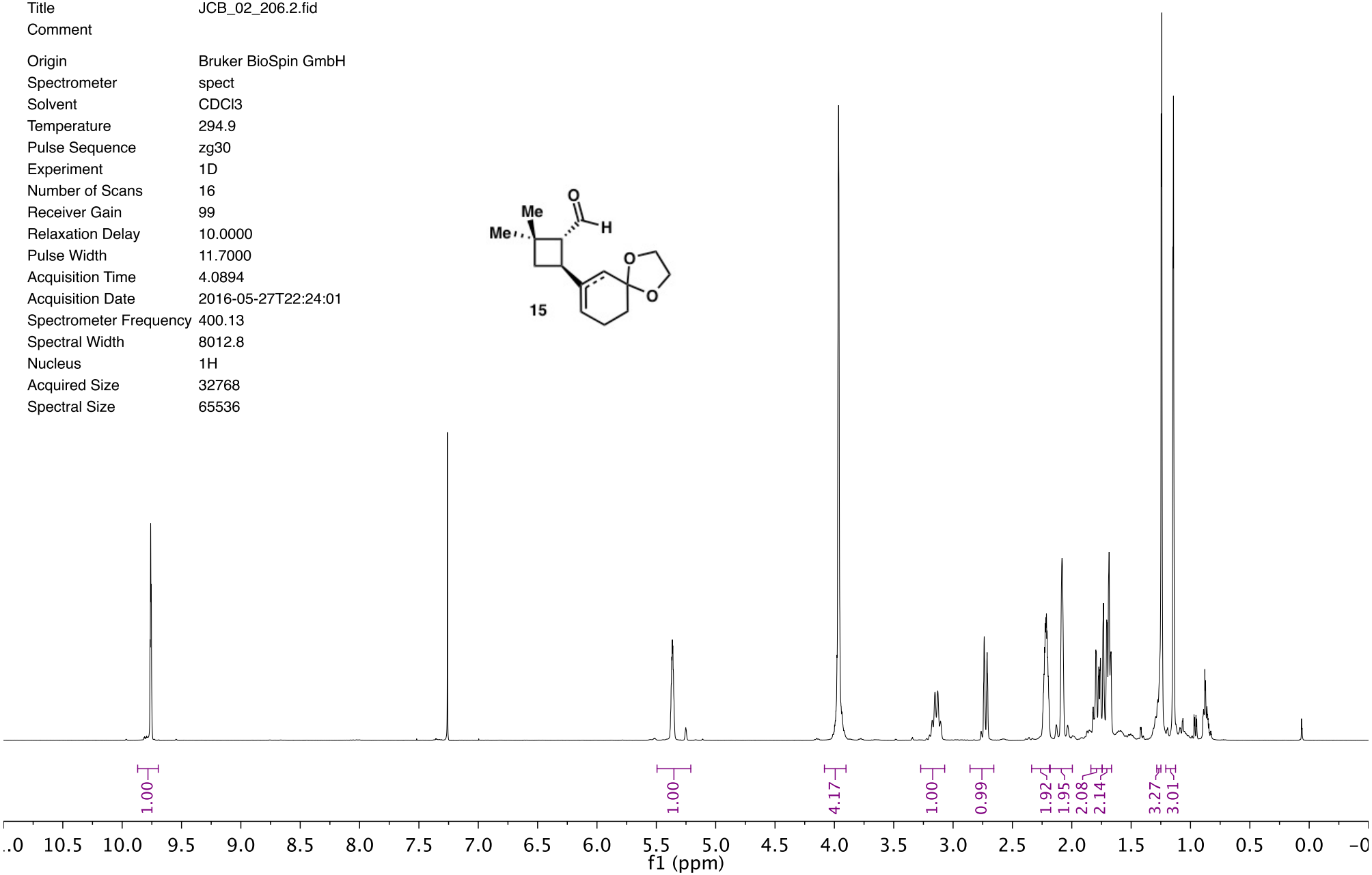
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ jbeck/ nmr/ JCB_02_211_P2/ 3/ fid
Title	JCB_02_211_P2.3.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	768
Receiver Gain	79
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-04T01:39:21
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

14



JCB_02_206.2.fid

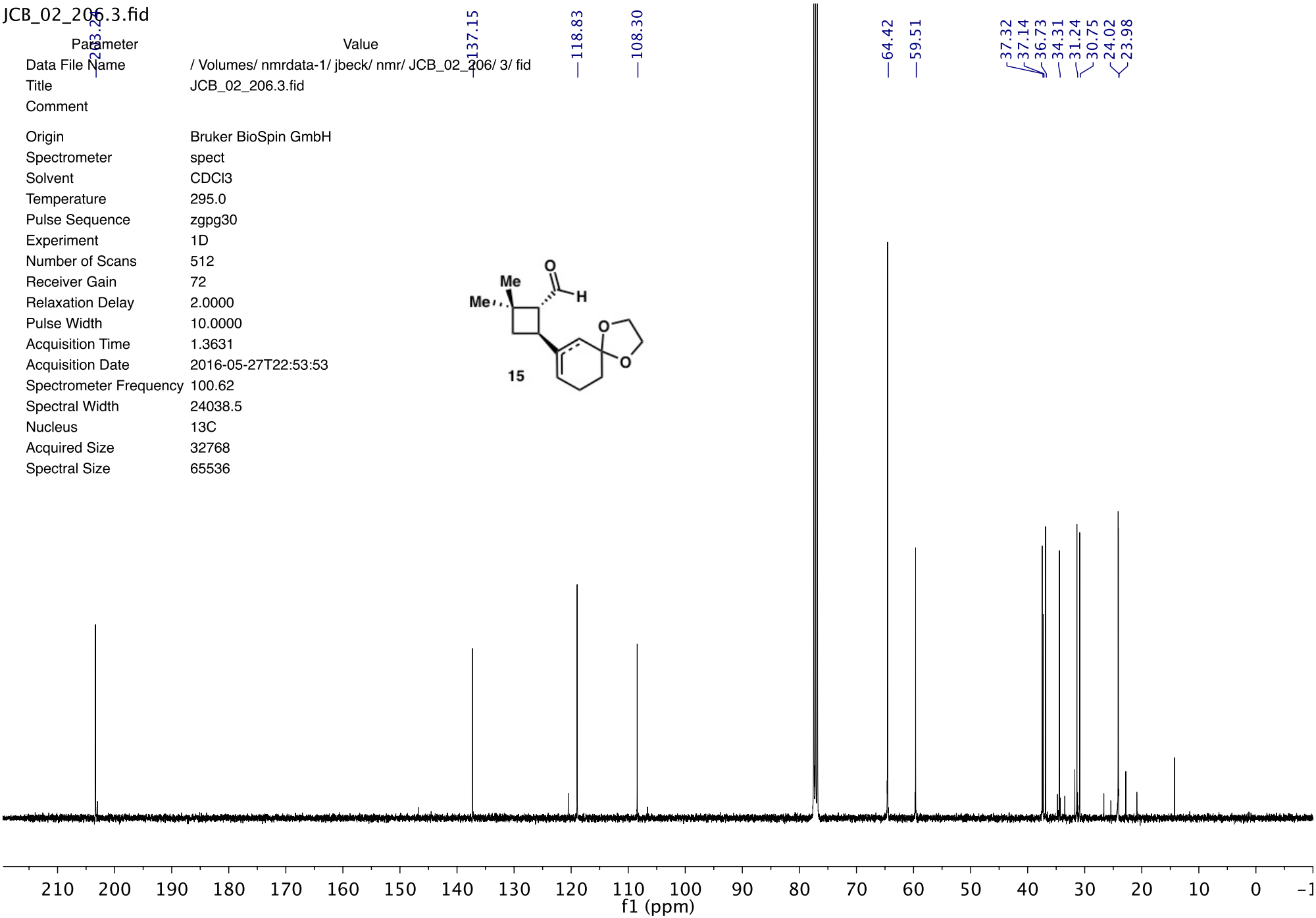
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ jbeck/ nmr/ JCB_02_206/ 2/ fid
Title	JCB_02_206.2.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	99
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-05-27T22:24:01
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



JCB_02_206.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ jbeck/ nmr/ JCB_02_206/ 3/ fid
Title	JCB_02_206.3.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	512
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-05-27T22:53:53
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

15



JCB-02-207-vinylenone.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ JCB-02-207-vinylenone/ 1/ fid
Title	JCB-02-207-vinylenone.1.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	79
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-05-28T20:39:59
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

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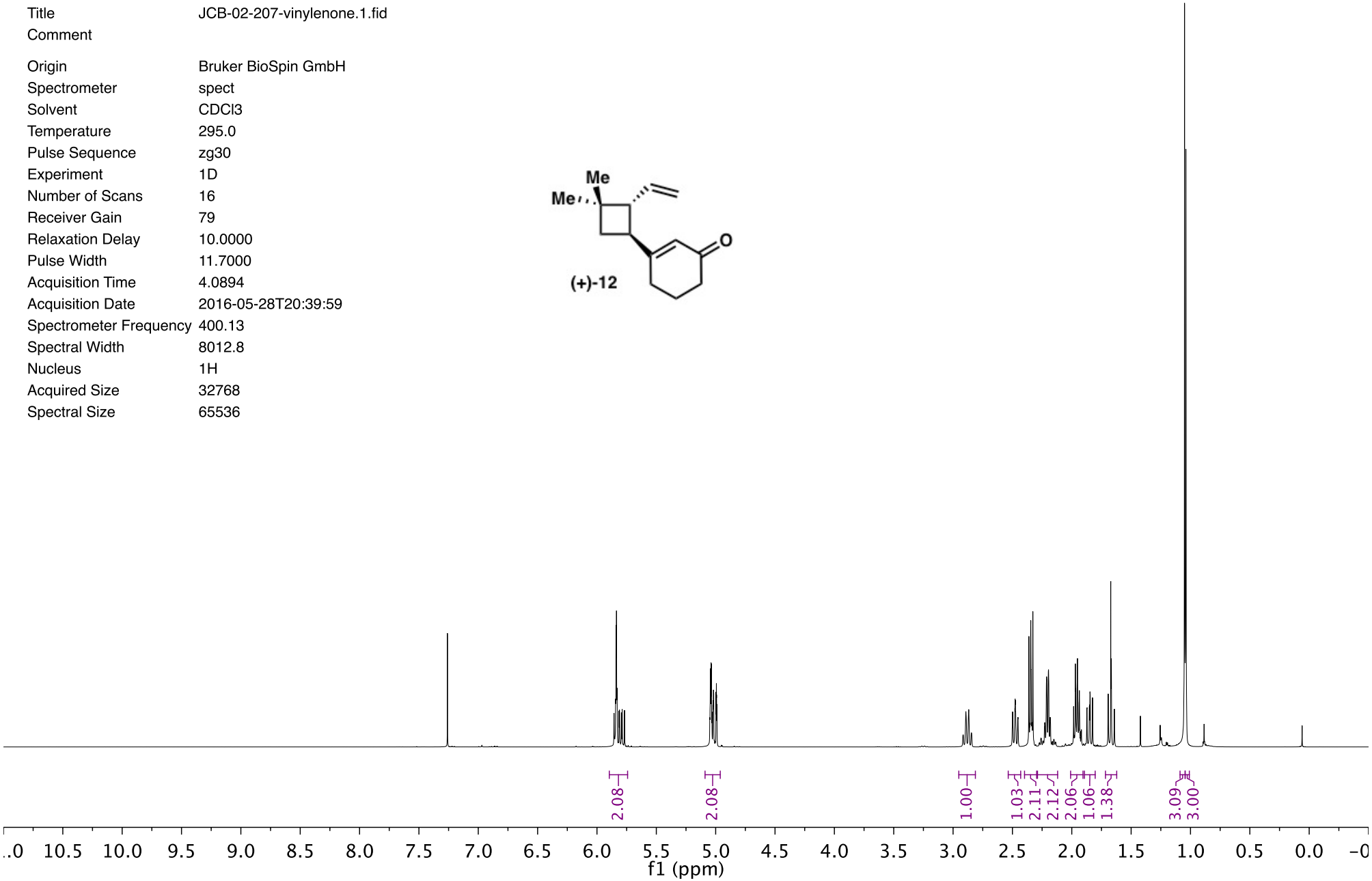
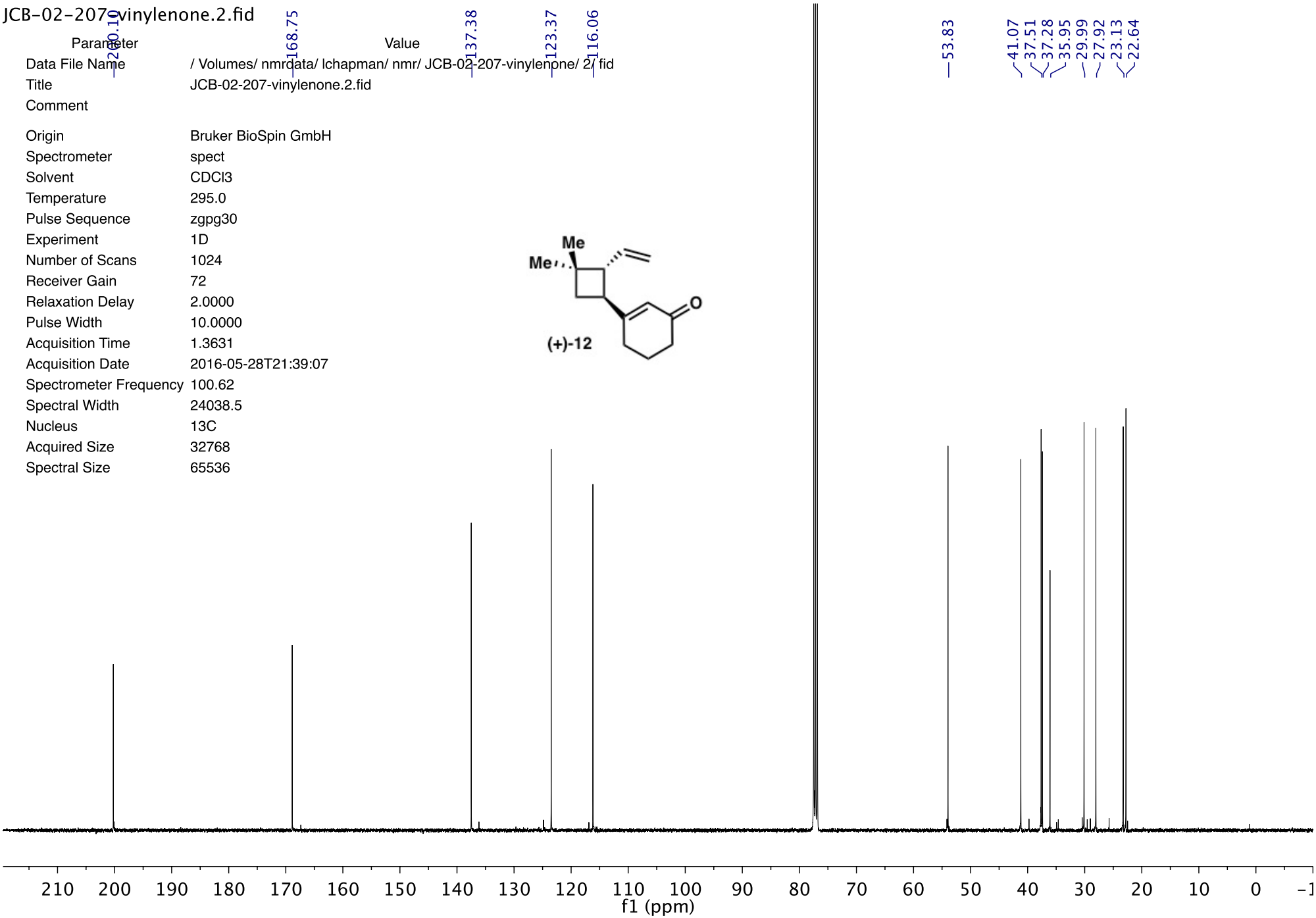


JCB-02-207-vinylenone.2.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ JCB-02-207-vinylenone/ 2/ fid
Title	JCB-02-207-vinylenone.2.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1024
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-05-28T21:39:07
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

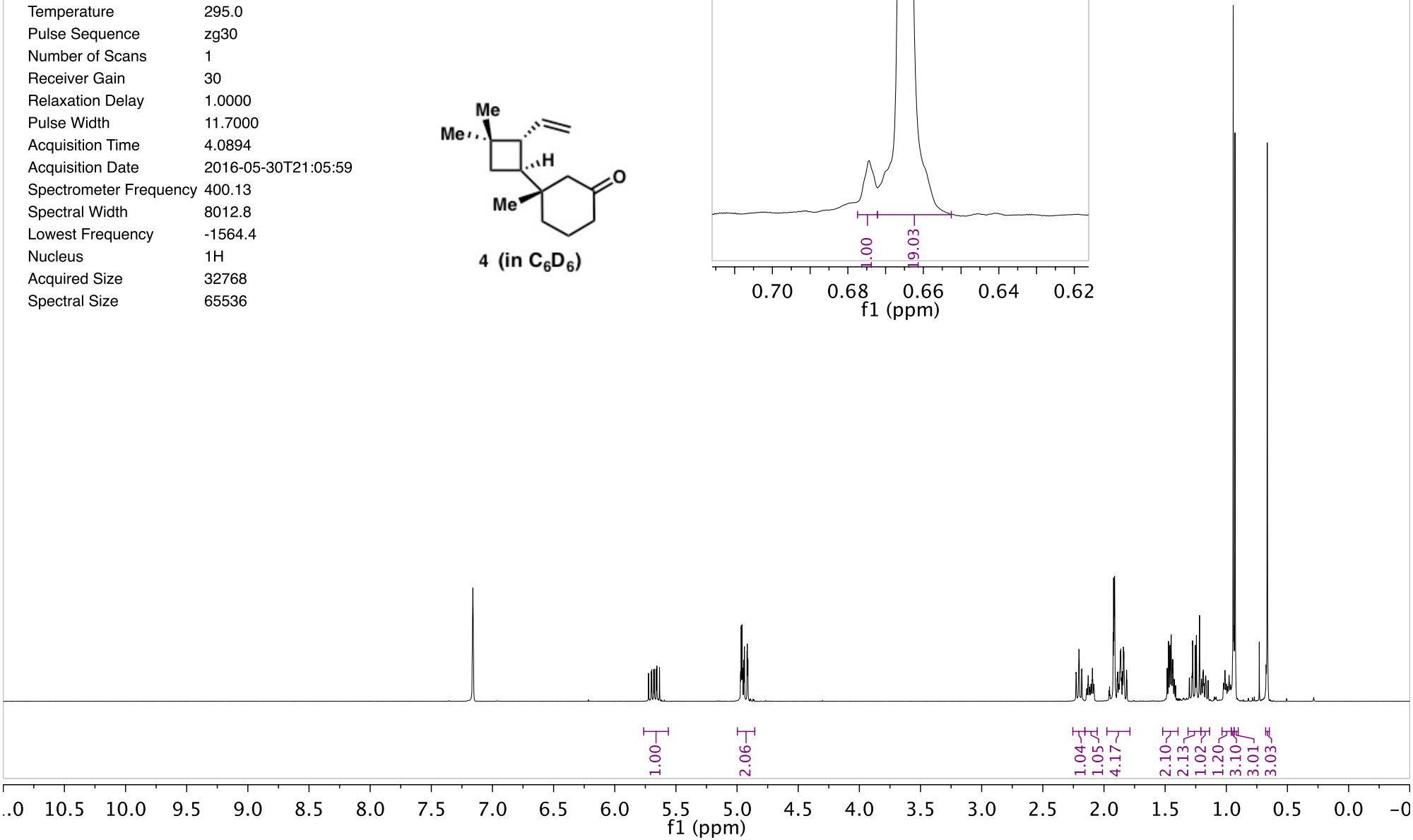
(+)-12



LMC-04-186-C6D6.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-186-C6D6/ 1/ fid
Title	LMC-04-186-C6D6.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-05-30T21:05:59
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1564.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

4 (in C_6D_6)

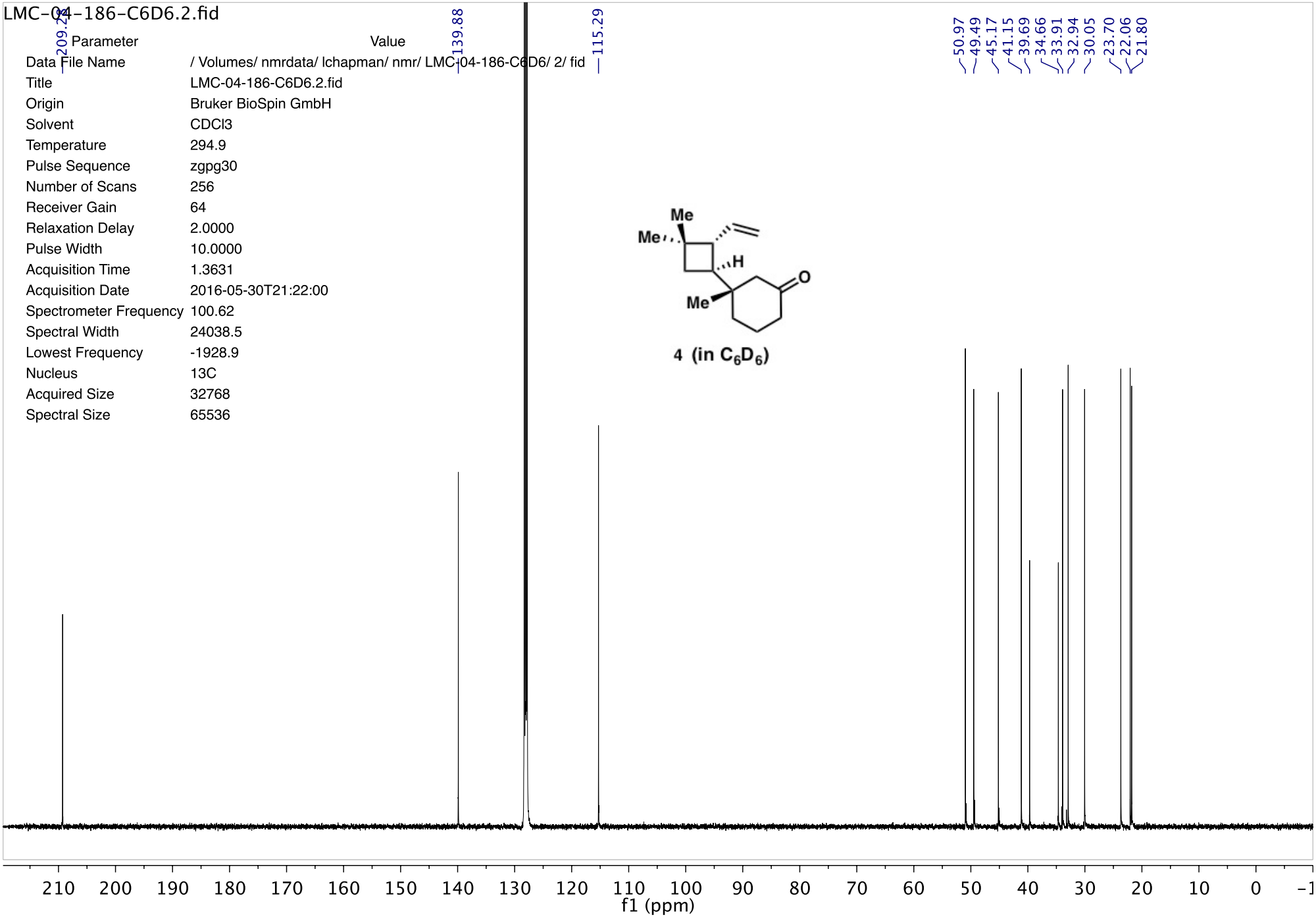


LMC-04-186-C6D6.2.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-186-C6D6/ 2/ fid
Title	LMC-04-186-C6D6.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	64
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-05-30T21:22:00
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1928.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

209.24
139.88
115.29
50.97
49.49
45.17
41.15
39.69
34.66
33.91
32.94
30.05
23.70
22.06
21.80

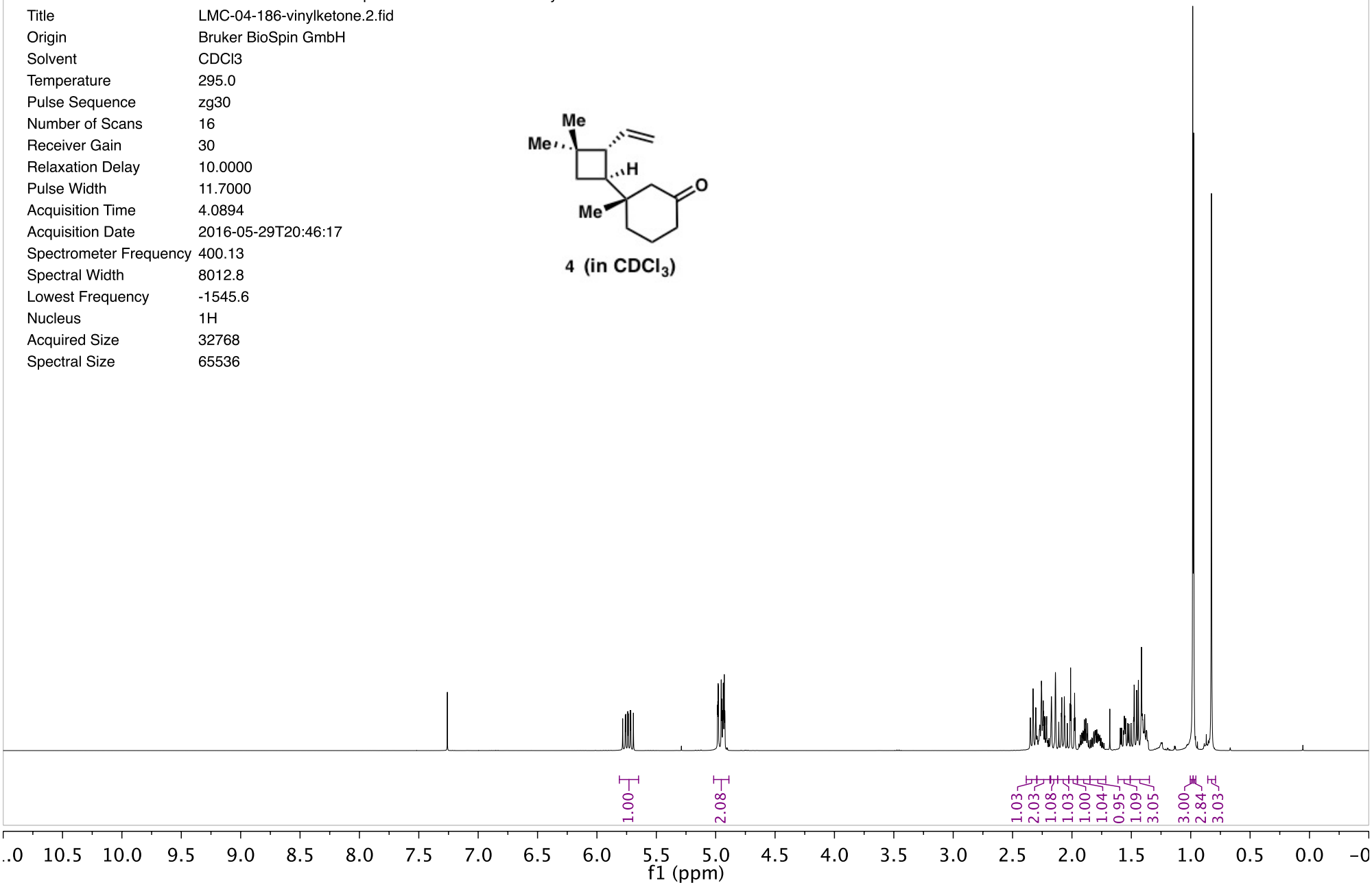
4 (in C_6D_6)



LMC-04-186-vinylketone.2.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-186-vinylketone/ 2/ fid
Title	LMC-04-186-vinylketone.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	30
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-05-29T20:46:17
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

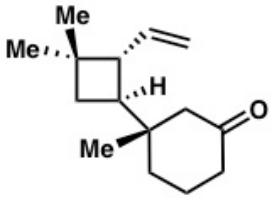
4 (in $CDCl_3$)



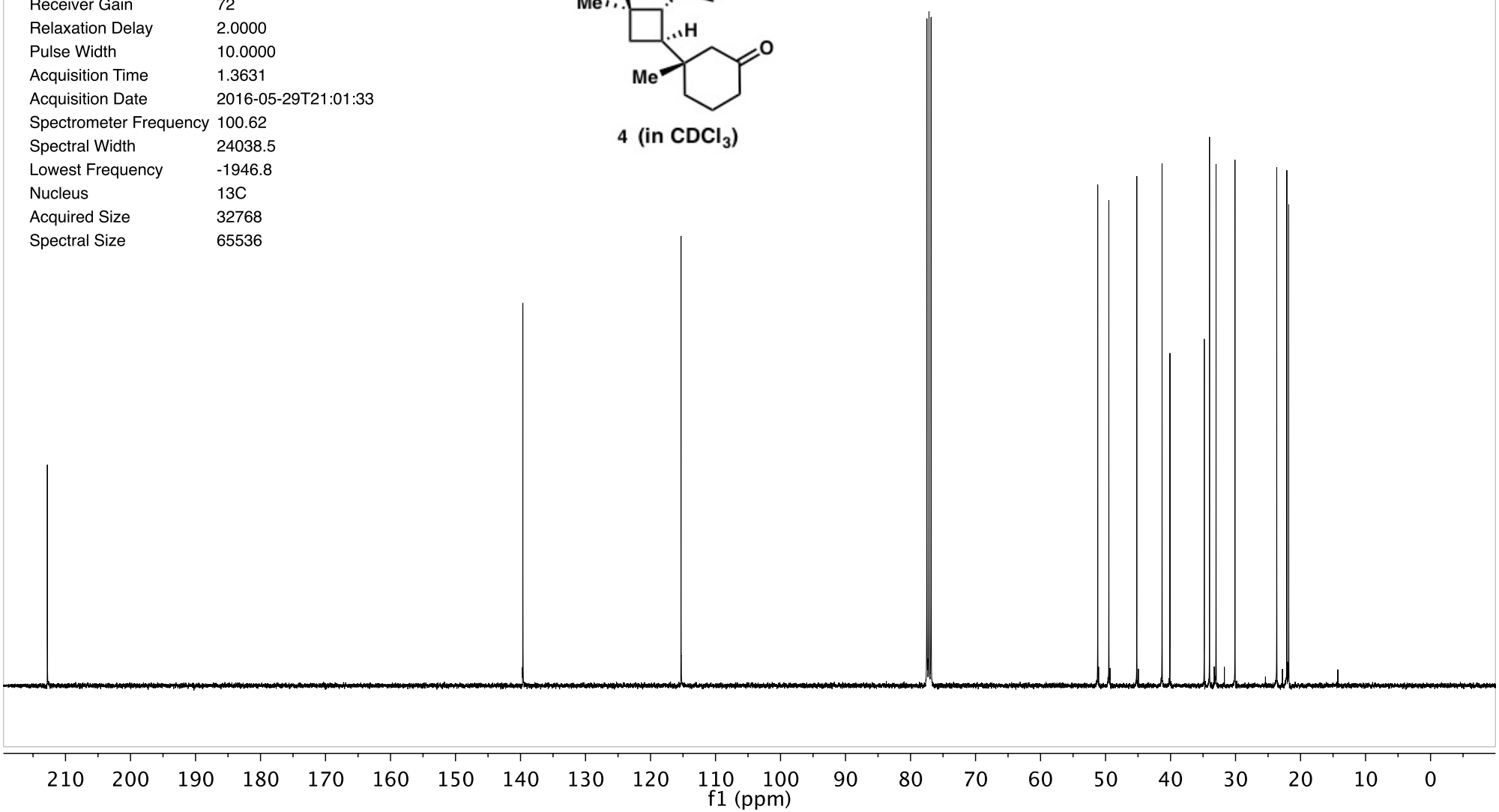
LMC-04-186-vinylketone.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-186-vinylketone/ 3/ fid
Title	LMC-04-186-vinylketone.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-05-29T21:01:33
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1946.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

212.80
139.64
115.31
51.20
49.49
45.19
41.30
40.09
34.81
34.00
33.00
30.09
23.66
22.11
21.82



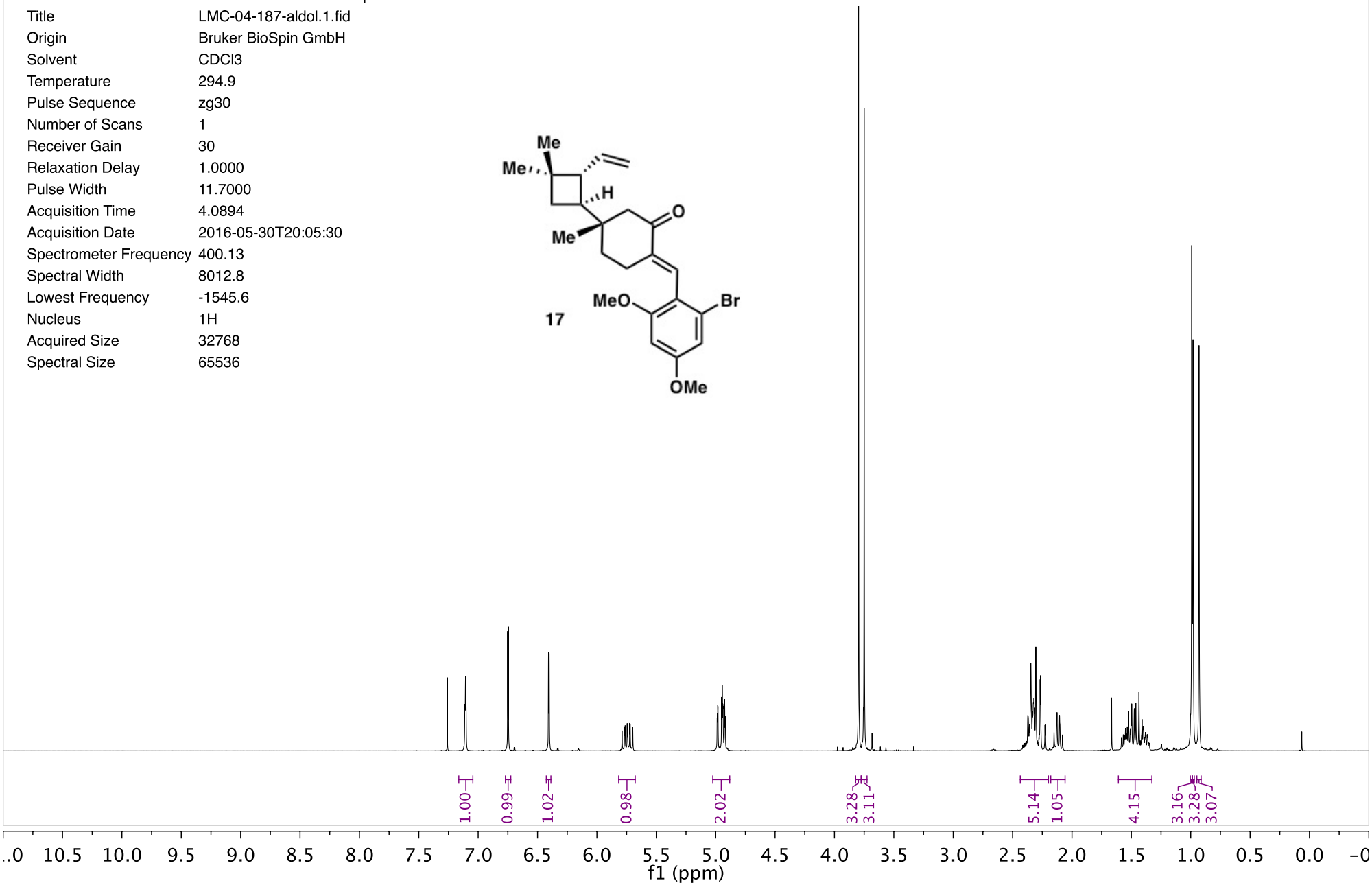
4 (in $CDCl_3$)



LMC-04-187-aldol.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-187-aldol/ 1/ fid
Title	LMC-04-187-aldol.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-05-30T20:05:30
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

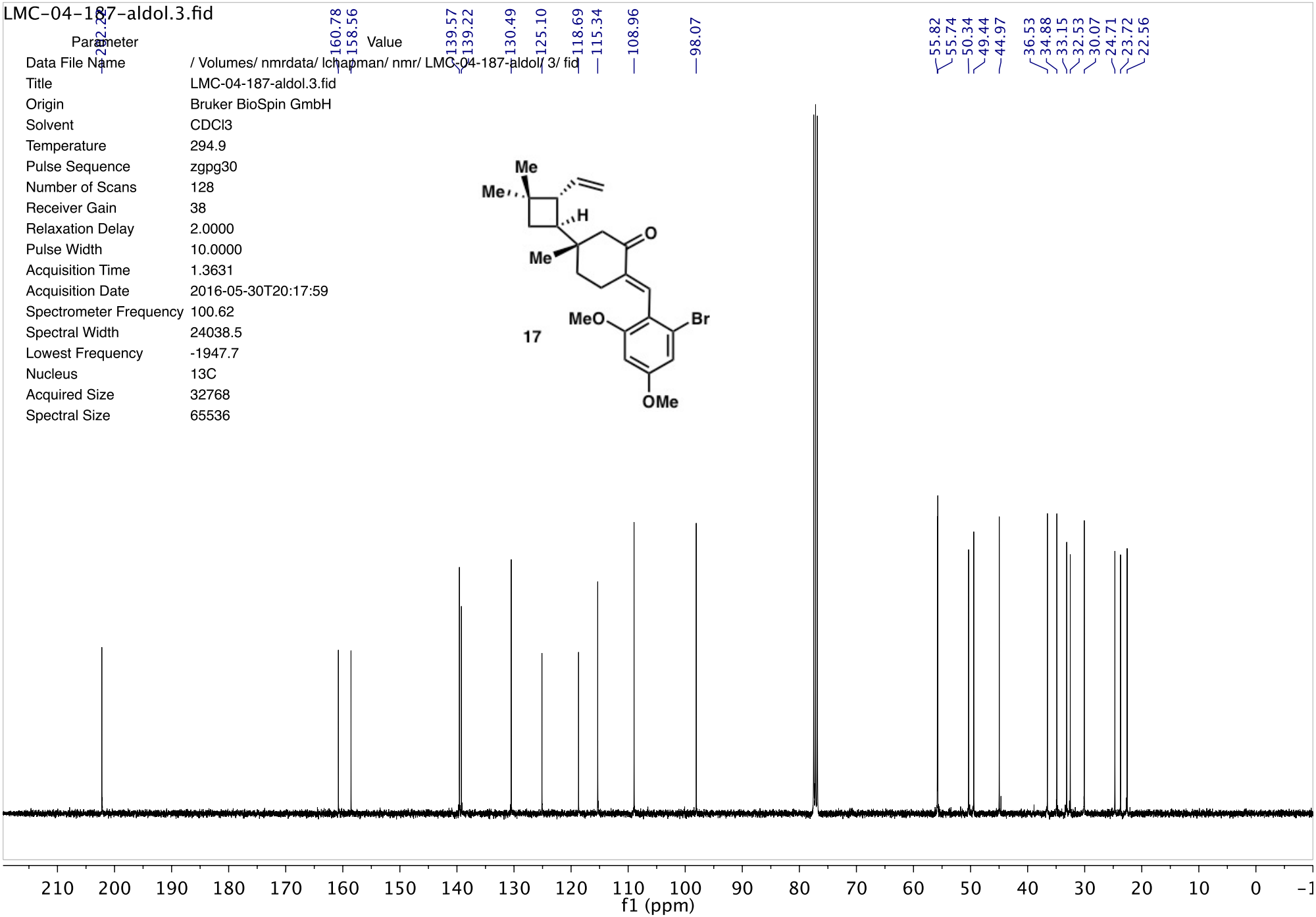
17



LMC-04-187-aldol.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-187-aldol/ 3/ fid
Title	LMC-04-187-aldol.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	38
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-05-30T20:17:59
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1947.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

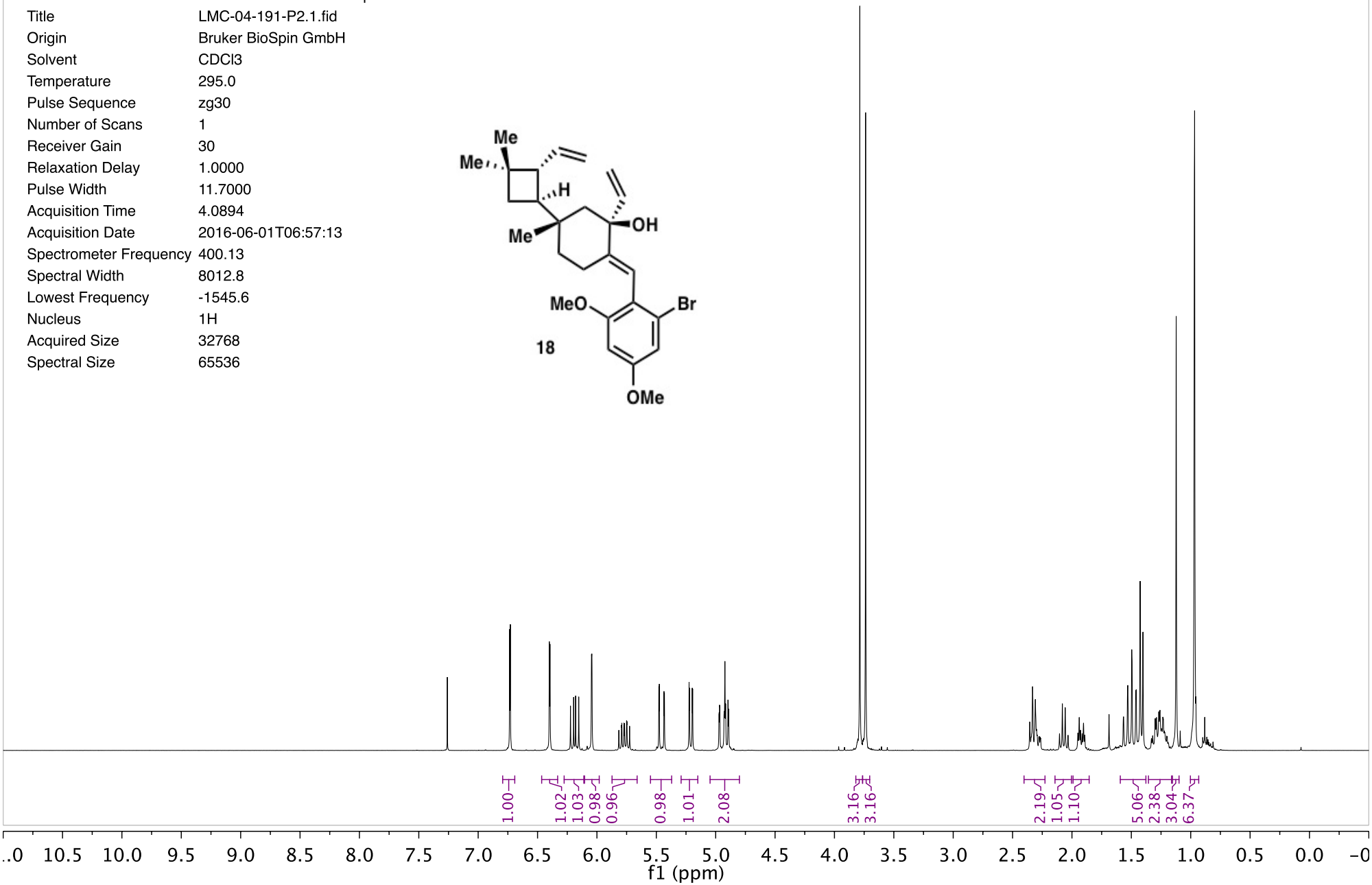
17



LMC-04-191-P2.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-191-P2/ 1/ fid
Title	LMC-04-191-P2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-01T06:57:13
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

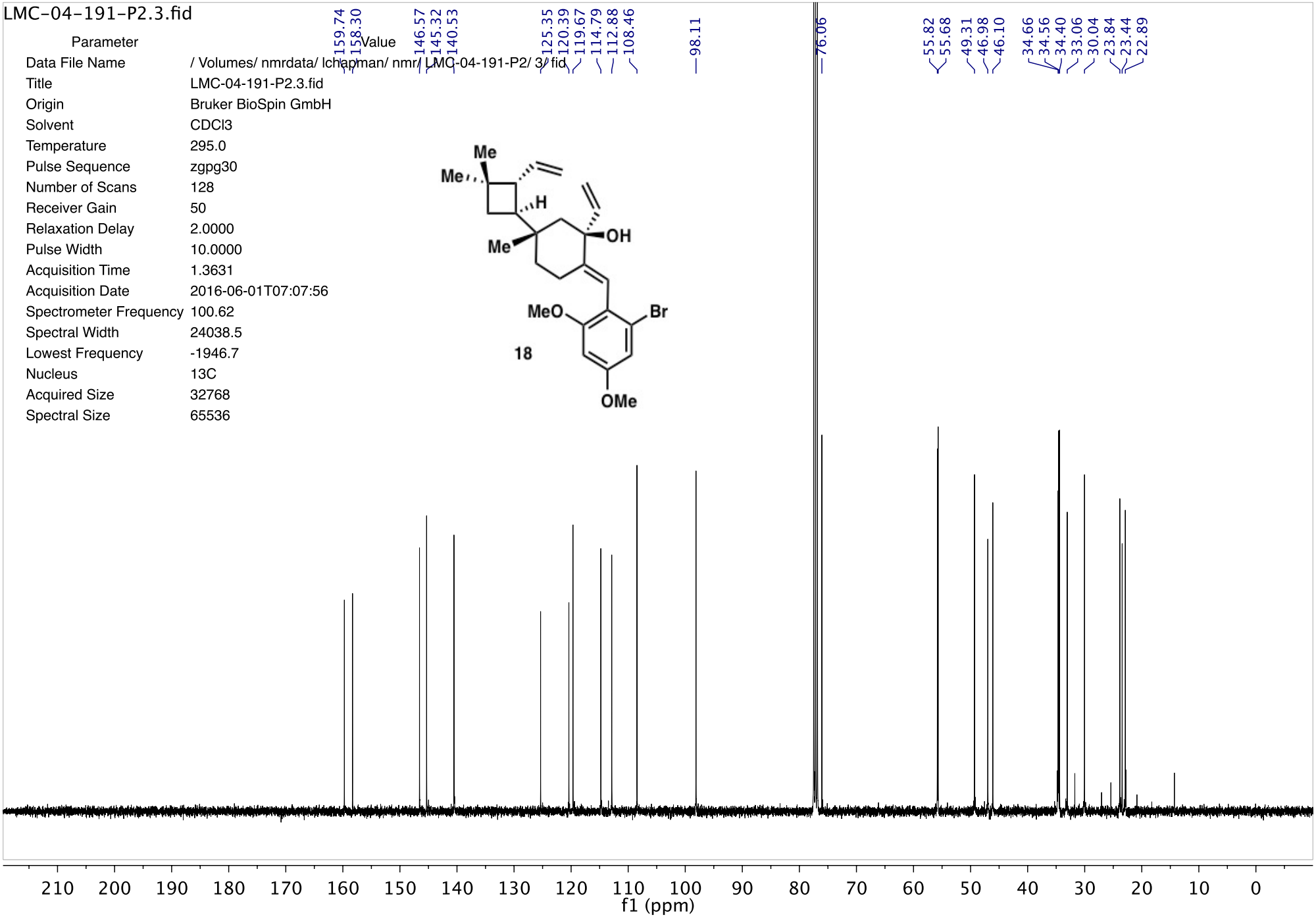
18



LMC-04-191-P2.3.fid

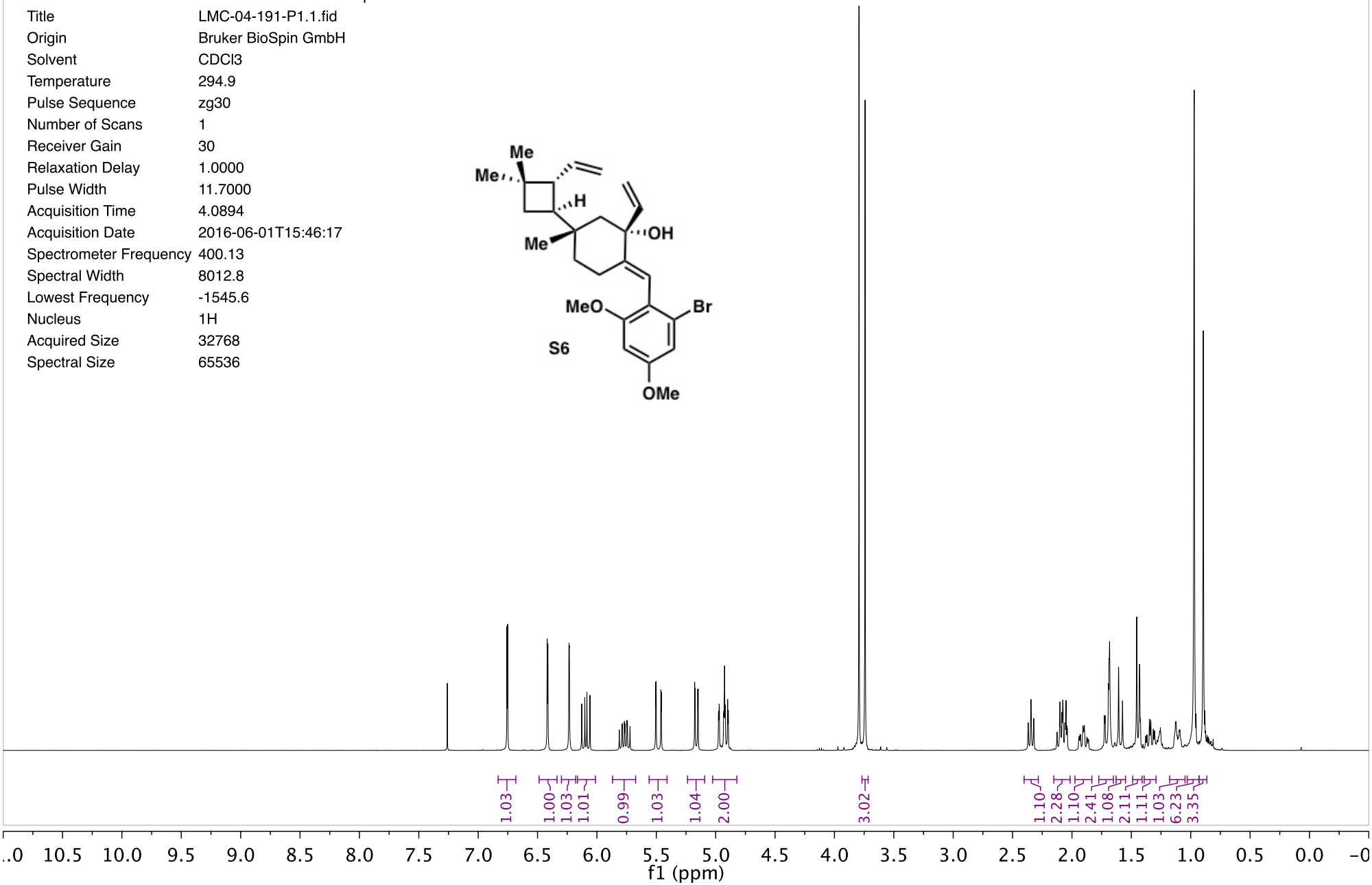
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-191-P2/ 3/ fid
Title	LMC-04-191-P2.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	50
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-01T07:07:56
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1946.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

159.74, 158.30, 146.57, 145.32, 140.53, 125.35, 120.39, 119.67, 114.79, 112.88, 108.46, 98.11, 76.06, 55.82, 55.68, 49.31, 46.98, 46.10, 34.66, 34.56, 34.40, 33.06, 30.04, 23.84, 23.44, 22.89



LMC-04-191-P1.1.fid

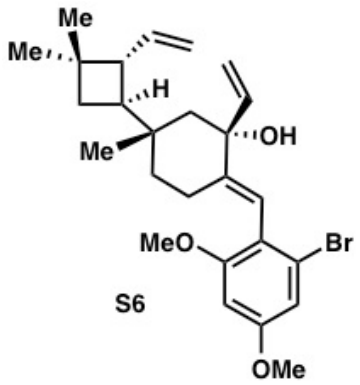
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-191-P1/ 1/ fid
Title	LMC-04-191-P1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-01T15:46:17
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



LMC-04-191-P1.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-191-P1/ 3/ fid
Title	LMC-04-191-P1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-01T16:03:15
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1947.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

159.63, 158.36, 146.23, 144.89, 140.59, 125.39, 120.87, 117.95, 115.60, 114.83, 108.43, 98.12, 75.83, 55.77, 55.68, 49.56, 49.13, 46.48, 35.60, 34.89, 34.54, 33.08, 30.05, 25.02, 23.82, 22.30

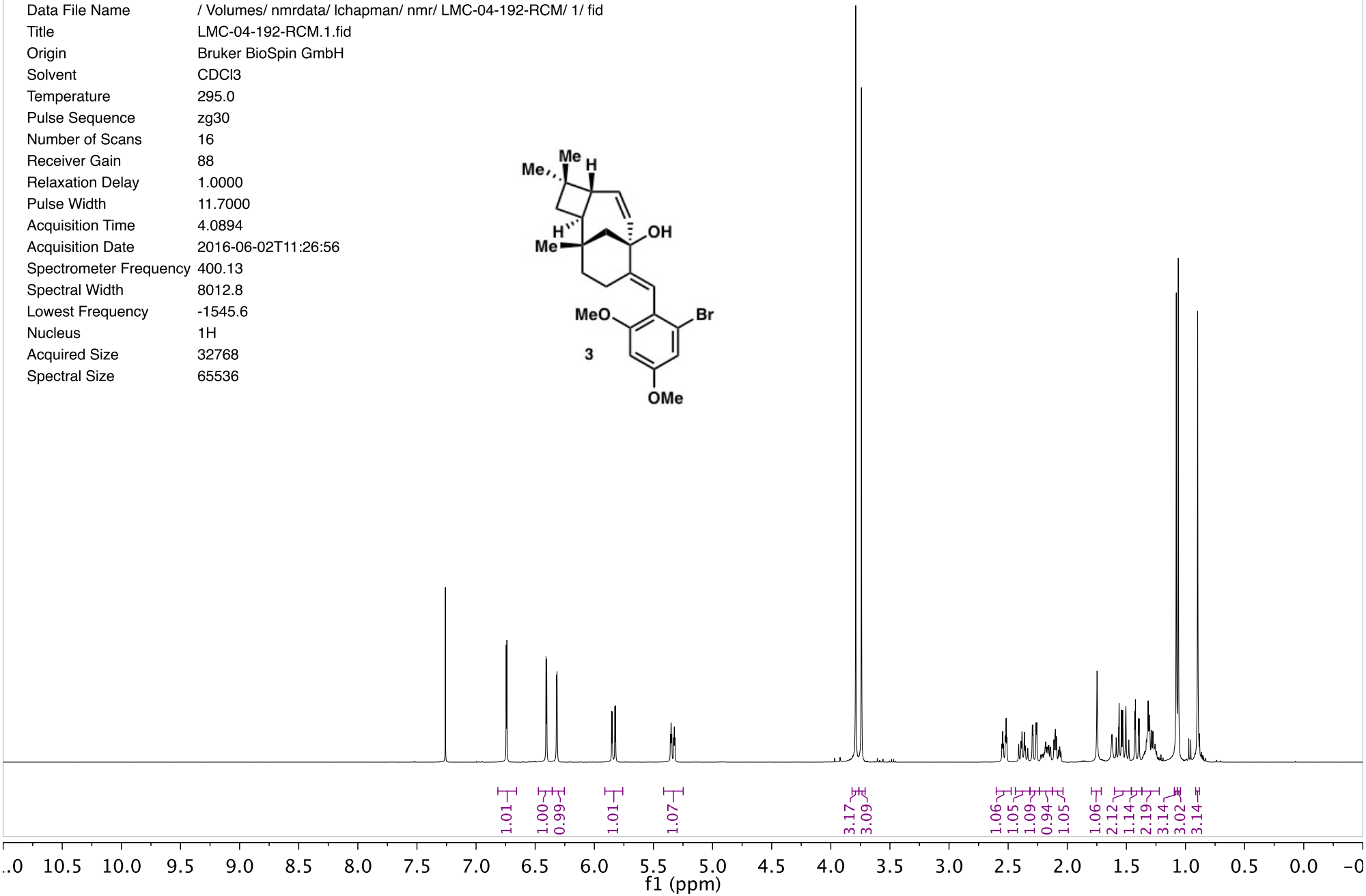


S6

f1 (ppm)

LMC-04-192-RCM.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-192-RCM/ 1/ fid
Title	LMC-04-192-RCM.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	88
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-02T11:26:56
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



LMC-04-192-RCM.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-192-RCM/ 3/ fid
Title	LMC-04-192-RCM.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-02T11:47:02
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1946.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

159.59
158.53
147.71
134.60
131.55
125.47
120.85
116.30
108.52
98.24
76.71
55.95
55.68
50.93
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43.44
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37.49
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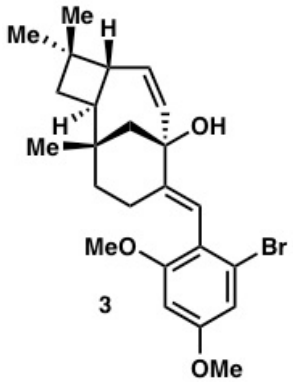
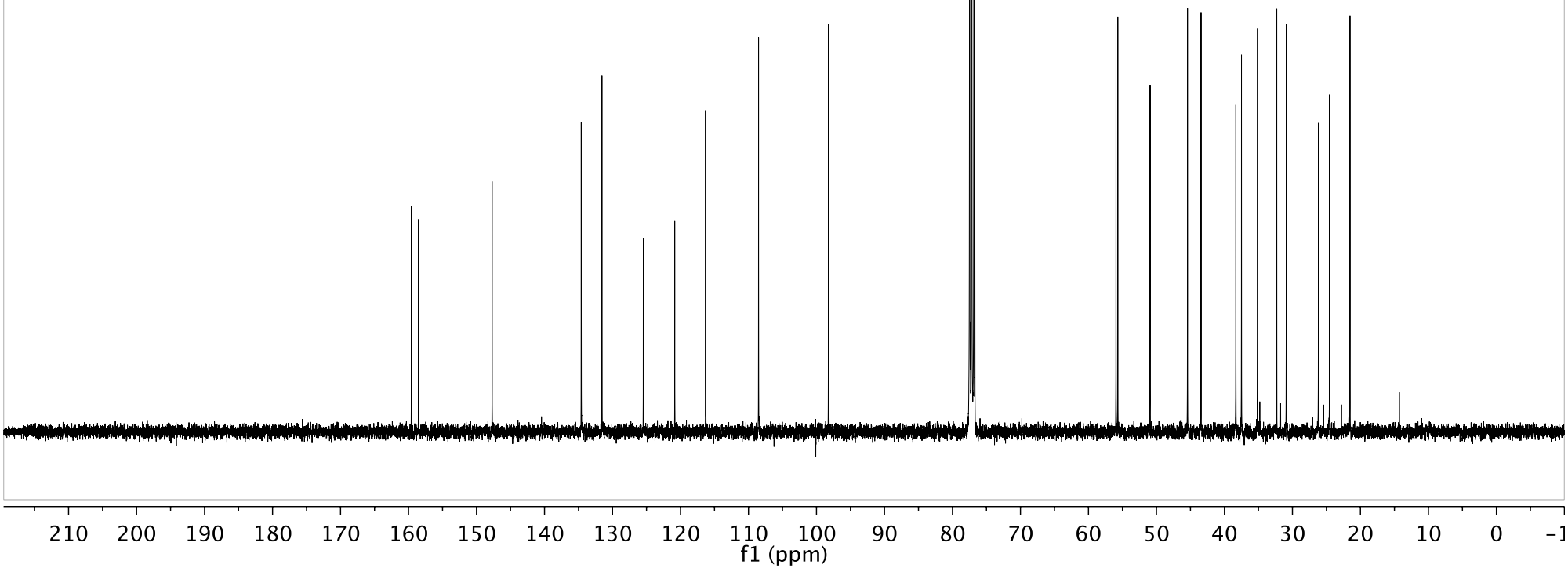
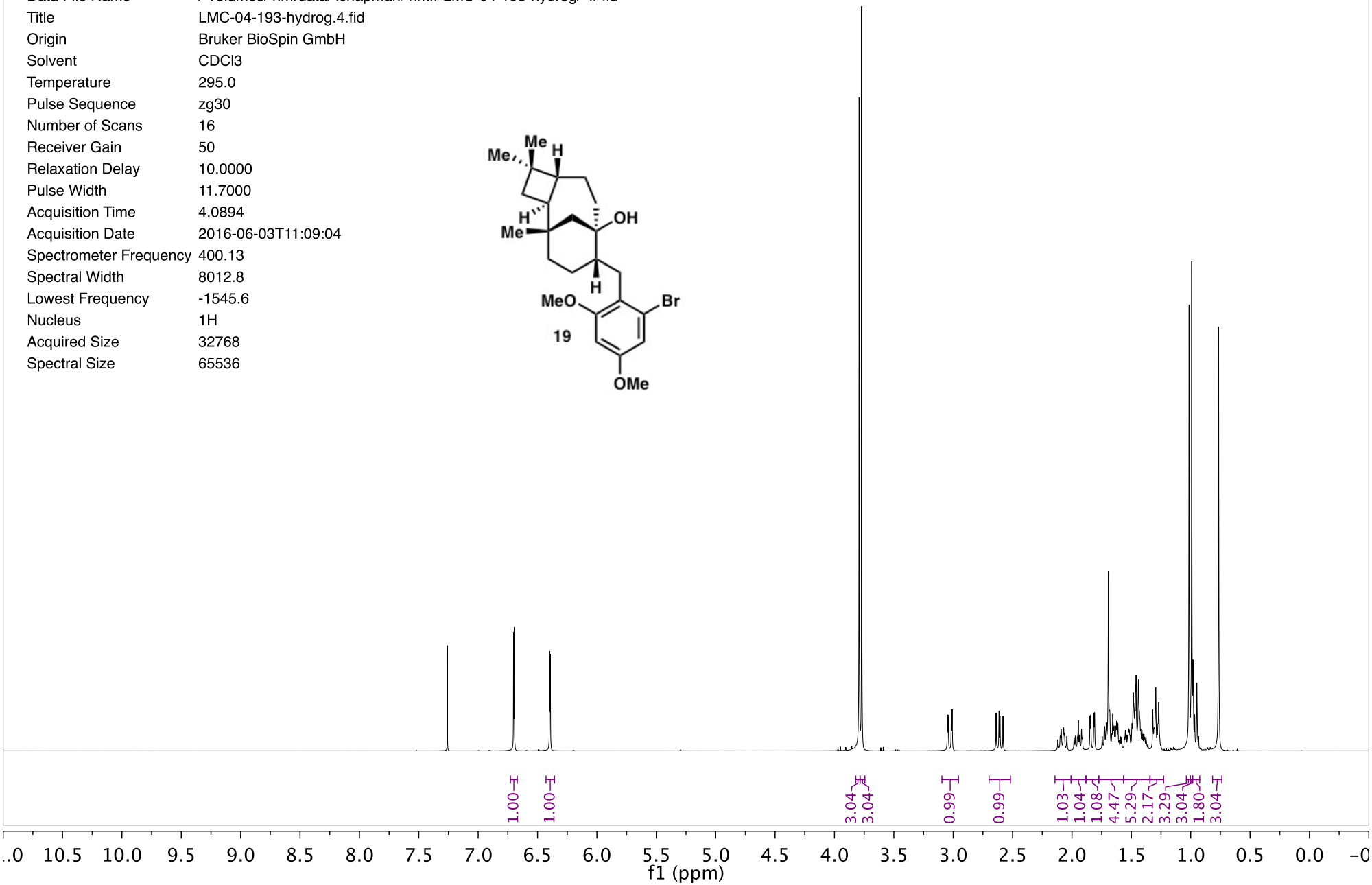
30.91
26.17
24.53
21.53





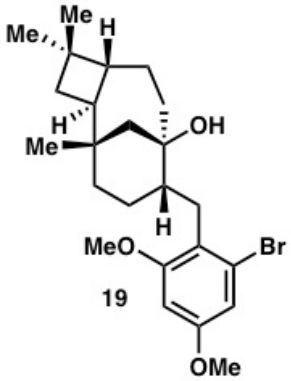
LMC-04-193-hydrog.4.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-193-hydrog/ 4/ fid
Title	LMC-04-193-hydrog.4.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	50
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-03T11:09:04
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



LMC-04-193-hydrog.5.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-193-hydrog/ 5/ fid
Title	LMC-04-193-hydrog.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	79
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-03T11:17:34
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1946.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

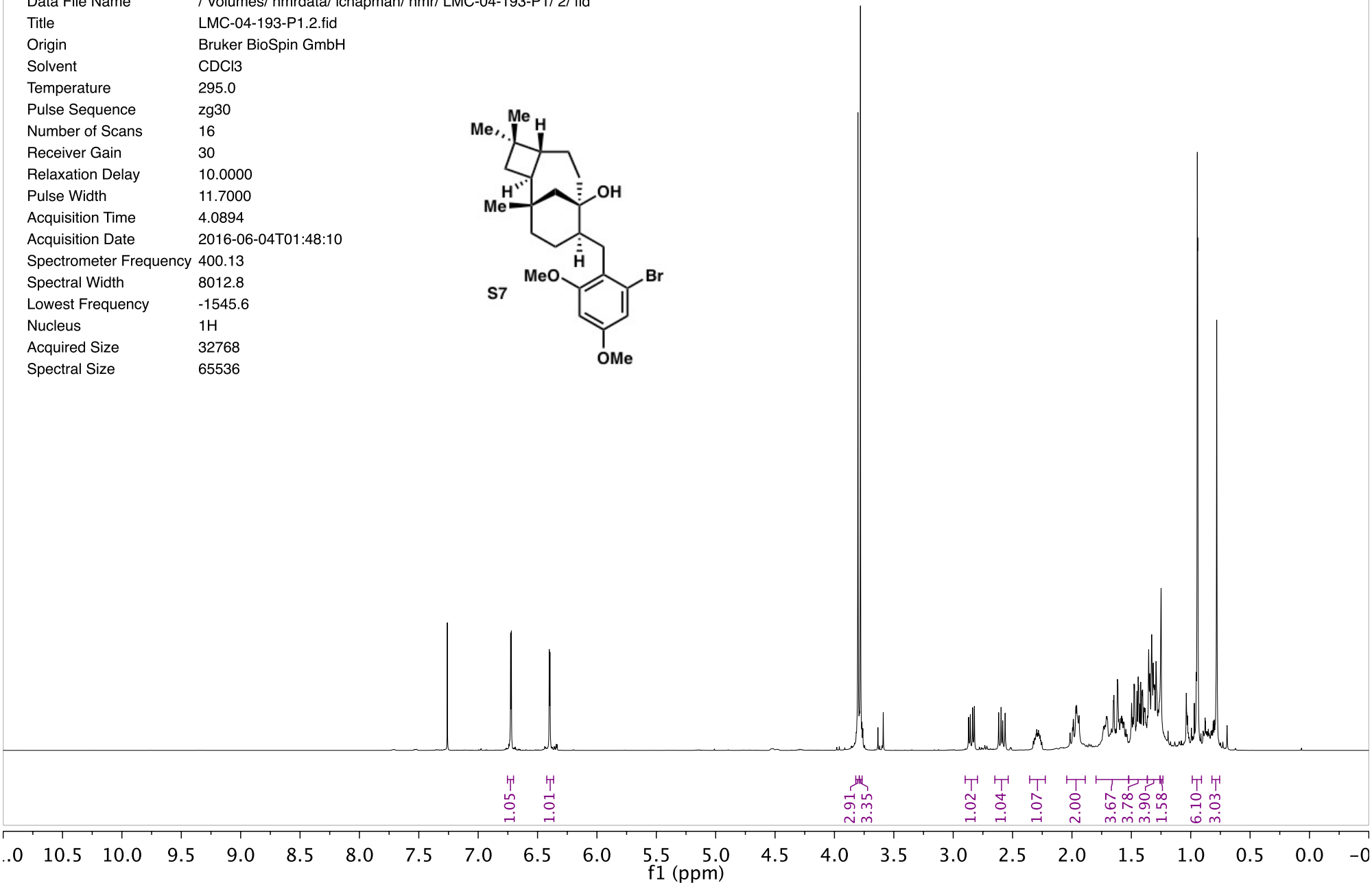


158.92
158.88
125.89
122.80
108.89
98.38
76.22
55.91
55.65
51.67
50.10
45.41
38.66
38.02
36.04
35.02
33.91
33.34
30.80
28.48
26.60
26.28
21.30
20.98

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

LMC-04-193-P1.2.fid

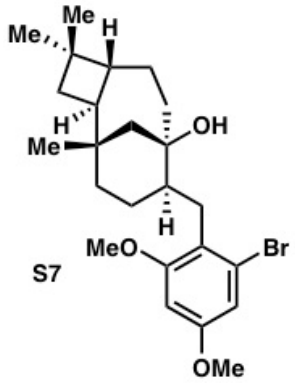
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-193-P1/ 2/ fid
Title	LMC-04-193-P1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	30
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-04T01:48:10
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



LMC-04-193-P1.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-193-P1/ 3/ fid
Title	LMC-04-193-P1.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	38
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-04T01:56:04
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1946.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

158.93
158.46
126.14
122.95
109.23
98.32
75.21
55.79
55.65
49.32
46.35
45.42
41.05
38.50
36.94
36.59
33.77
30.52
30.42
29.20
27.61
24.19
24.14
21.47

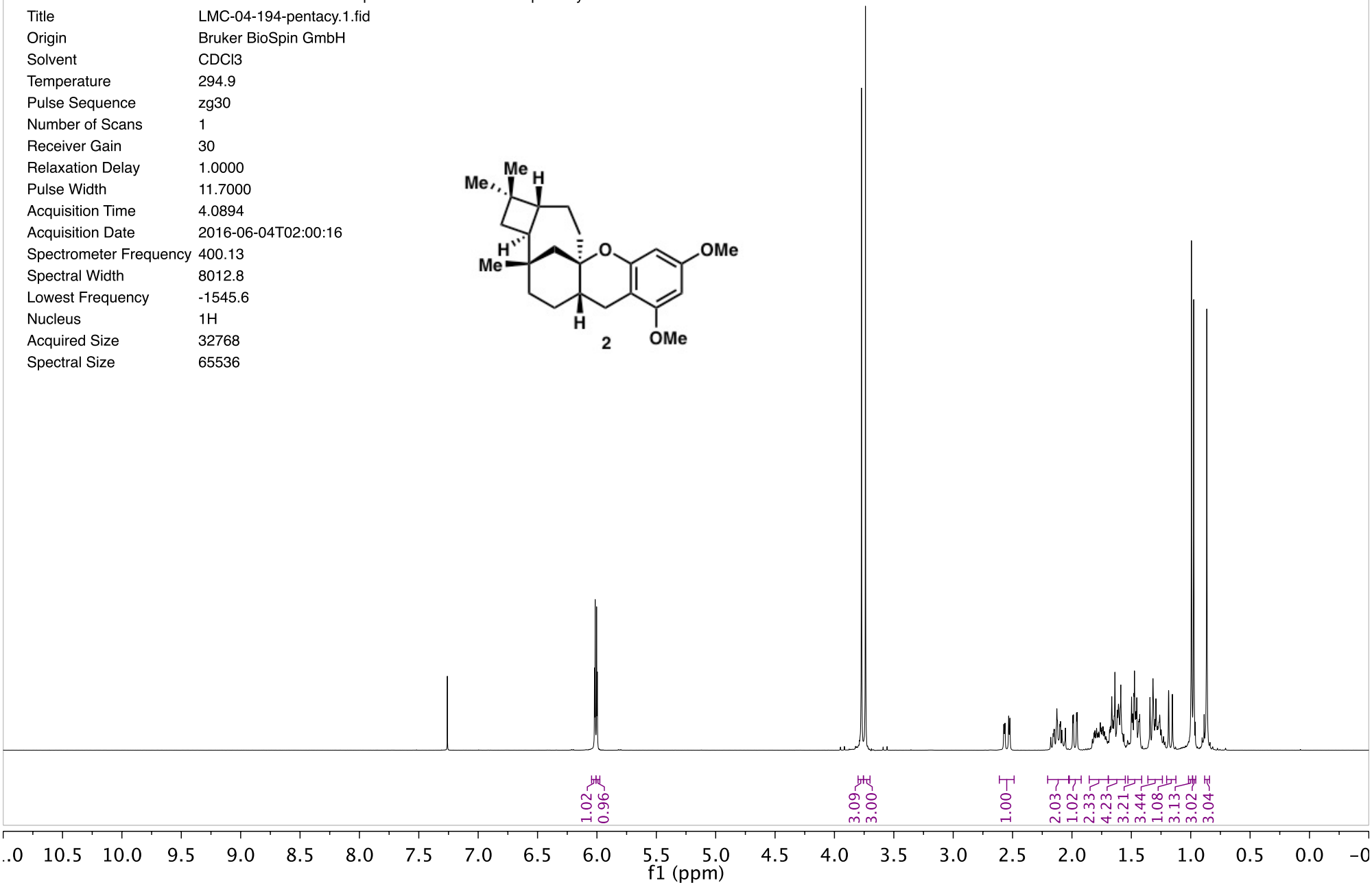


f1 (ppm)

LMC-04-194-pentacy.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-194-pentacy/ 1/ fid
Title	LMC-04-194-pentacy.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-04T02:00:16
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

2

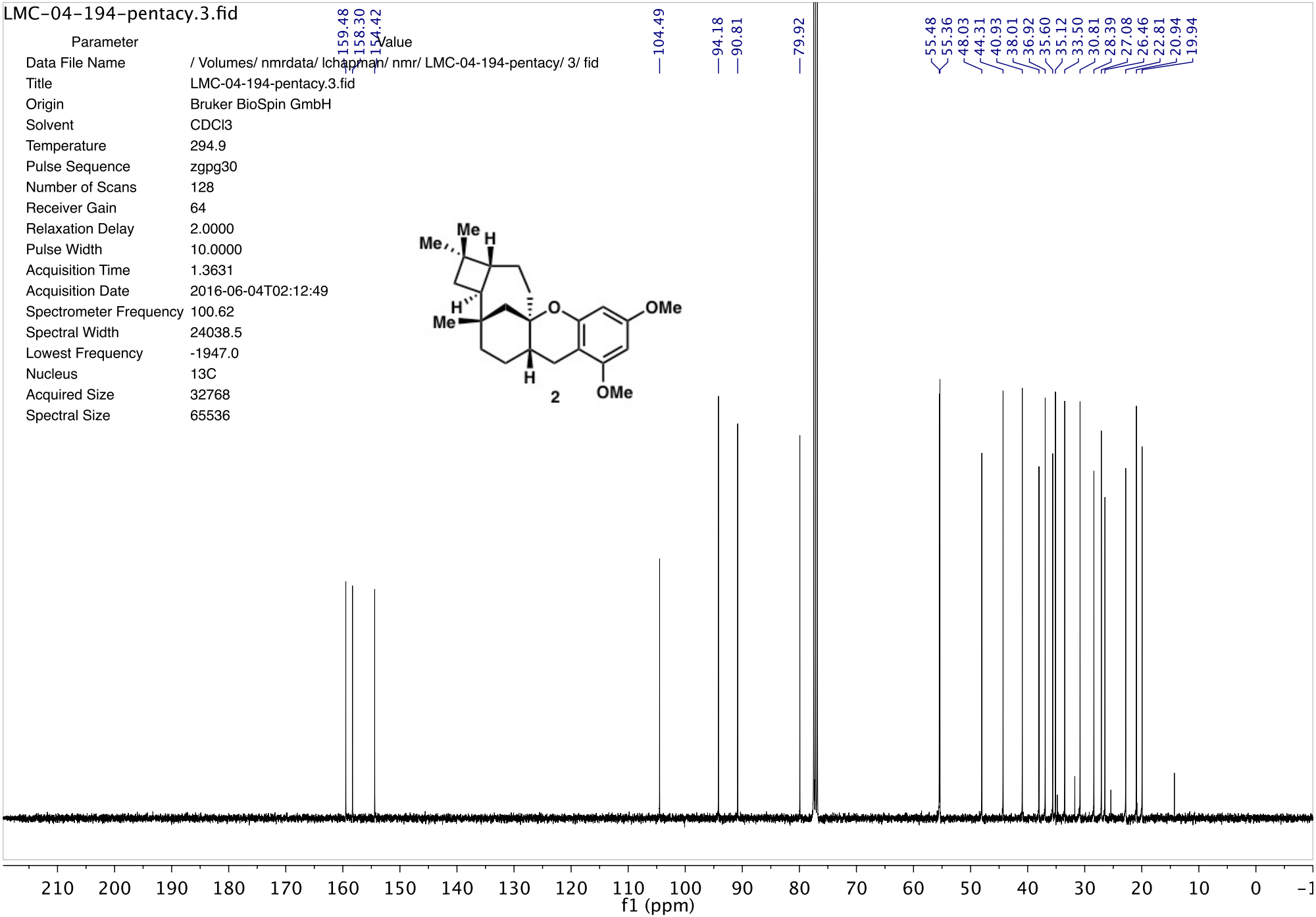


LMC-04-194-pentacy.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-194-pentacy/ 3/ fid
Title	LMC-04-194-pentacy.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	64
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-04T02:12:49
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1947.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

159.48
158.30
154.42
104.49
94.18
90.81
79.92
55.48
55.36
48.03
44.31
40.93
38.01
36.92
35.60
35.12
33.50
30.81
28.39
27.08
26.46
22.81
20.94
19.94

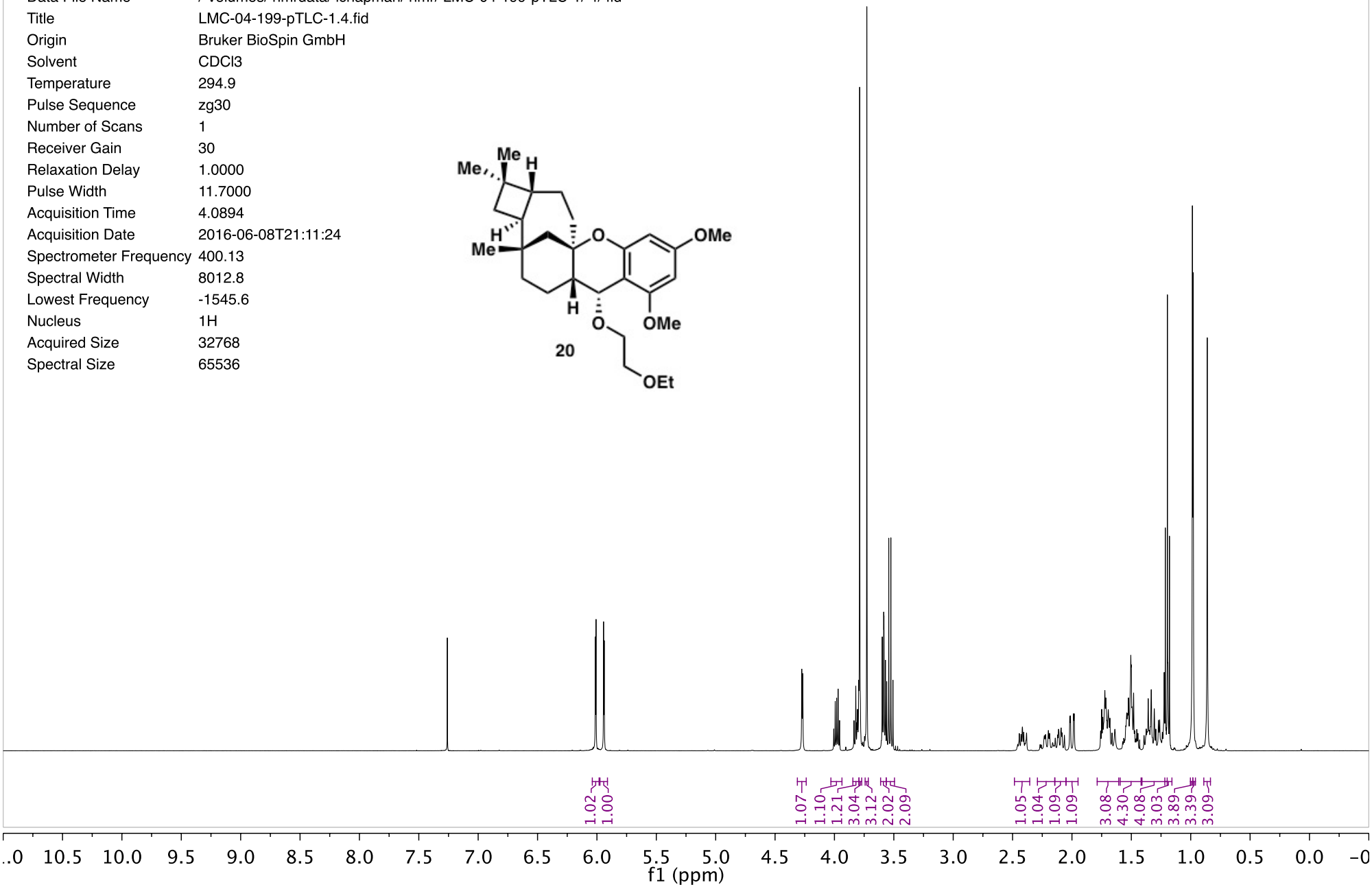
2



LMC-04-199-pTLC-1.4.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-199-pTLC-1/ 4/ fid
Title	LMC-04-199-pTLC-1.4.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-08T21:11:24
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

20

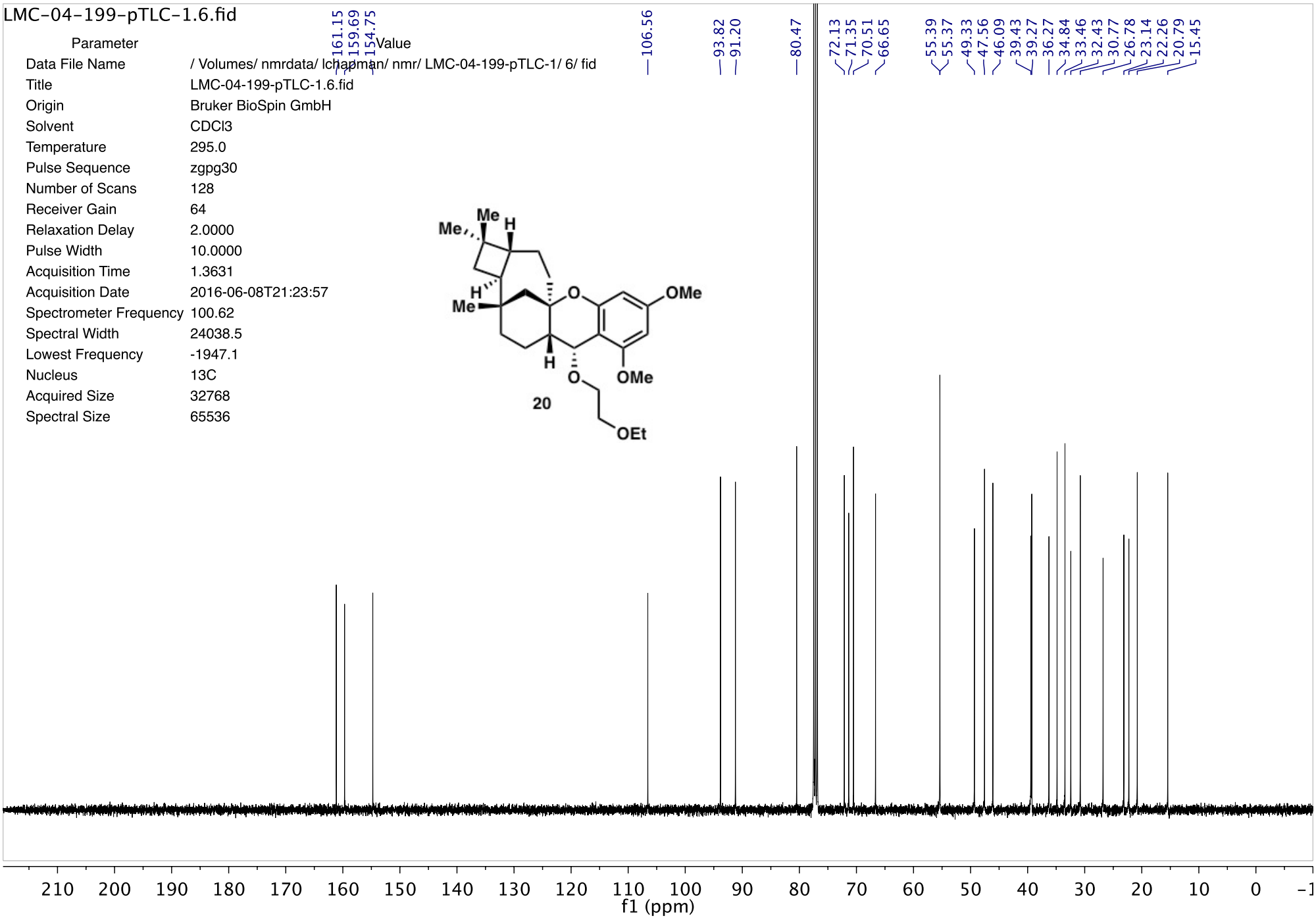


LMC-04-199-pTLC-1.6.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-199-pTLC-1/ 6/ fid
Title	LMC-04-199-pTLC-1.6.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	64
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-08T21:23:57
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1947.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

20

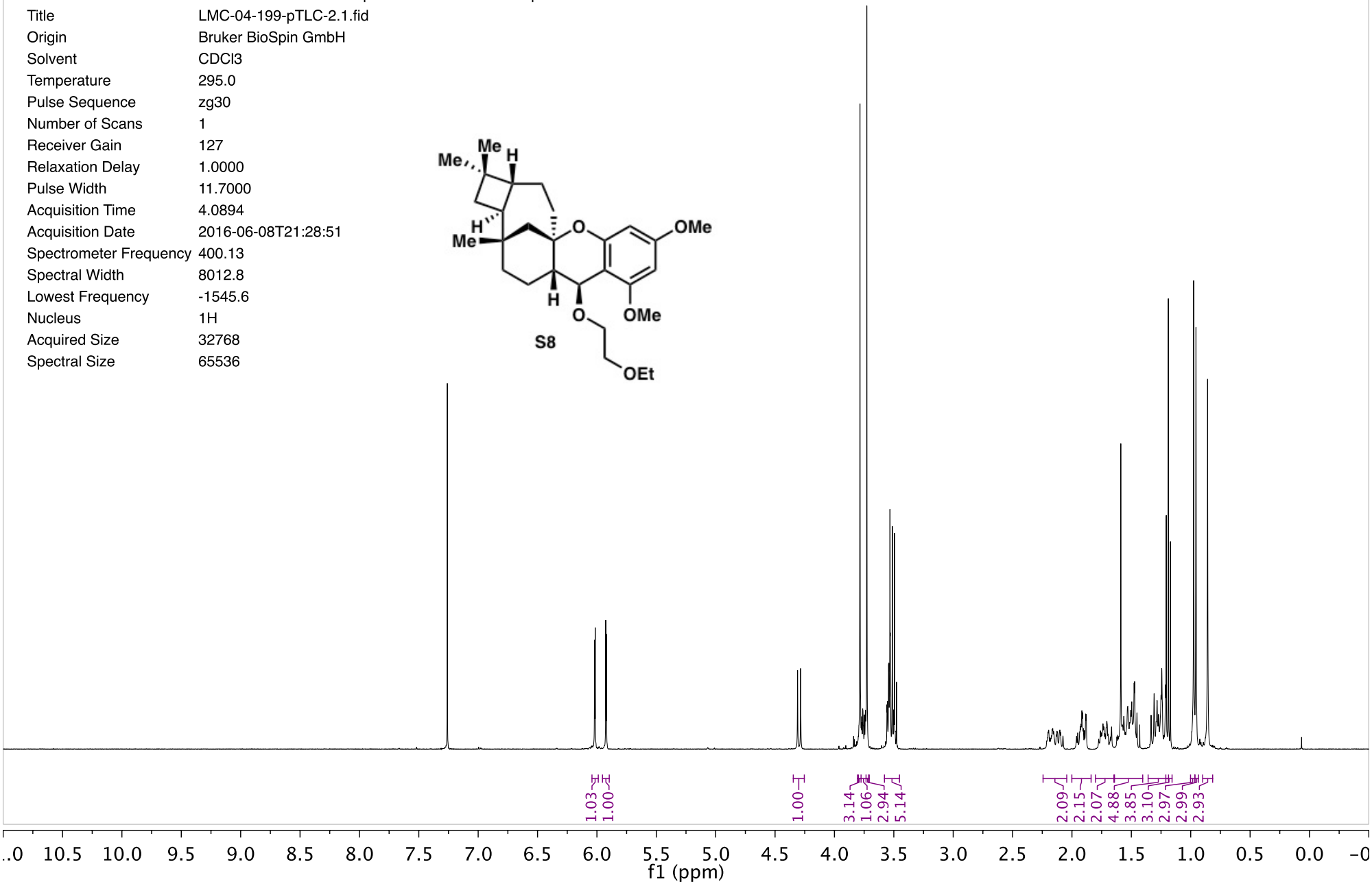
161.15
159.69
154.75
106.56
93.82
91.20
80.47
72.13
71.35
70.51
66.65
55.39
55.37
49.33
47.56
46.09
39.43
39.27
36.27
34.84
33.46
32.43
30.77
26.78
23.14
22.26
20.79
15.45



LMC-04-199-pTLC-2.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-199-pTLC-2/ 1/ fid
Title	LMC-04-199-pTLC-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	127
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-08T21:28:51
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

S8

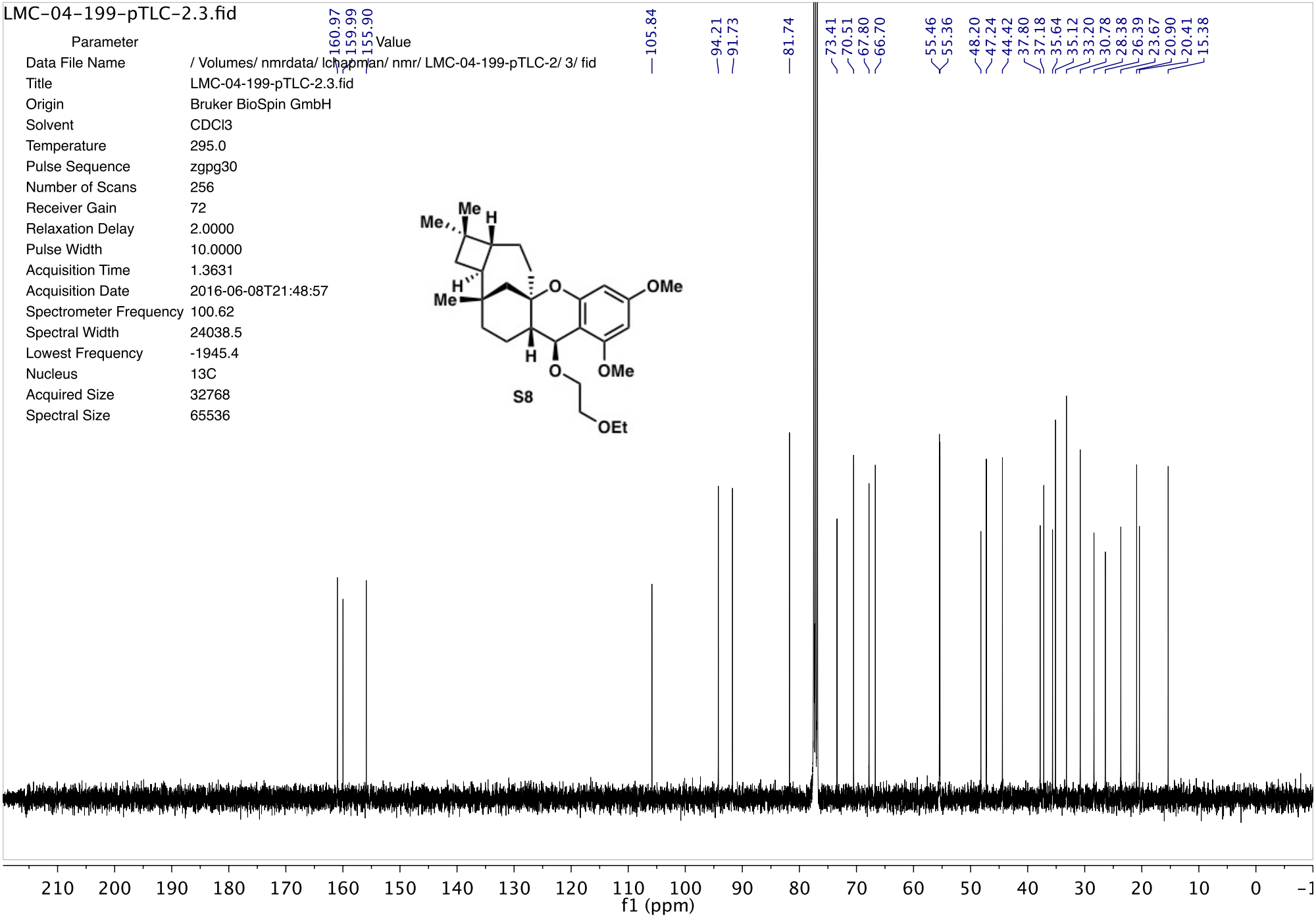


LMC-04-199-pTLC-2.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-199-pTLC-2/ 3/ fid
Title	LMC-04-199-pTLC-2.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-08T21:48:57
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1945.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

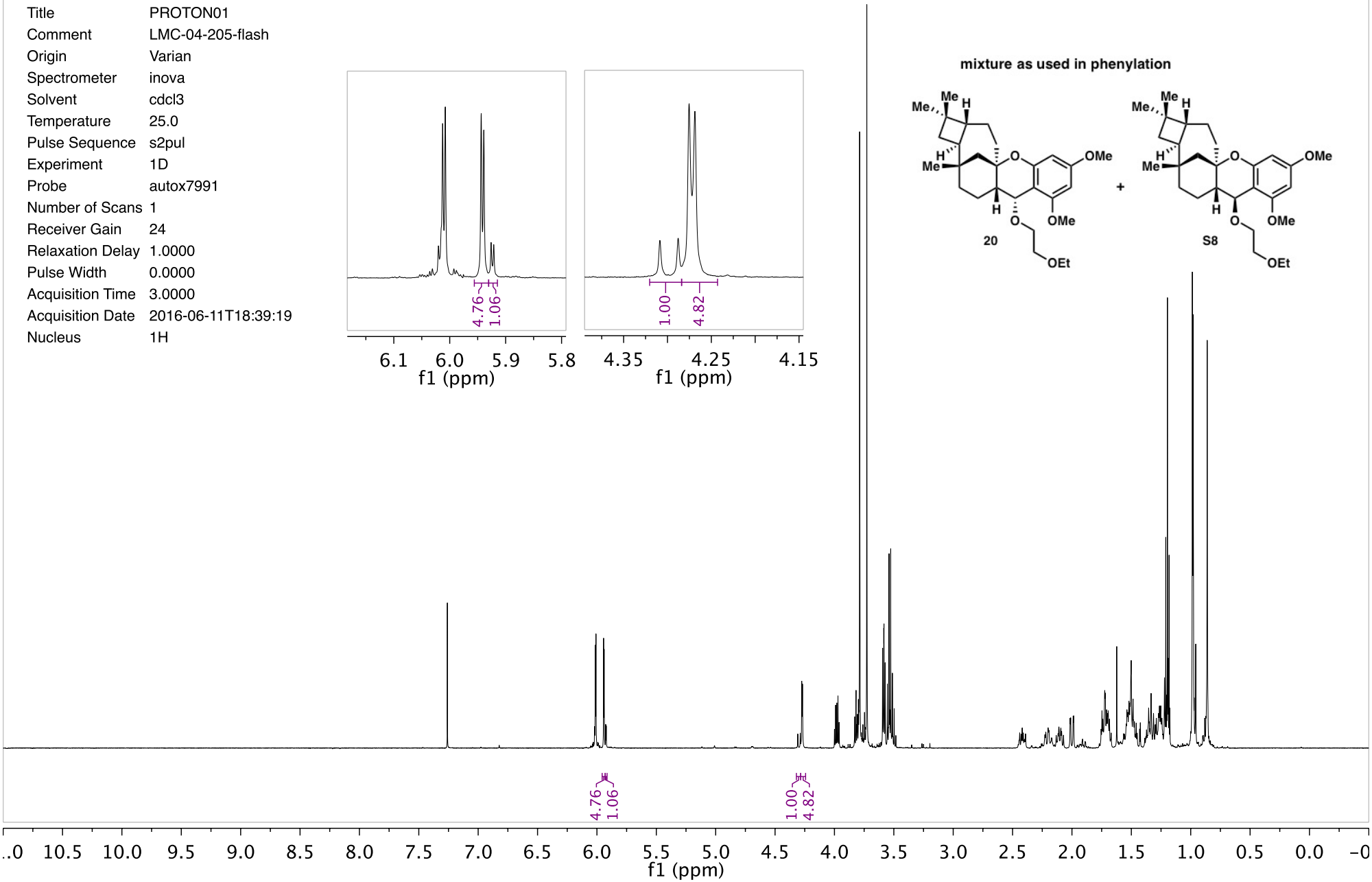
S8

160.97
159.99
155.90
105.84
94.21
91.73
81.74
73.41
70.51
67.80
66.70
55.46
55.36
48.20
47.24
44.42
37.80
37.18
35.64
35.12
33.20
30.78
28.38
26.39
23.67
20.90
20.41
15.38



PROTON01
LMC-04-205-flash

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ lchapman/ vnmrsys/ data/ LMC-04-205-flash/ PROTON01.fid/ fid
Title	PROTON01
Comment	LMC-04-205-flash
Origin	Varian
Spectrometer	inova
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	autox7991
Number of Scans	1
Receiver Gain	24
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	3.0000
Acquisition Date	2016-06-11T18:39:19
Nucleus	1H



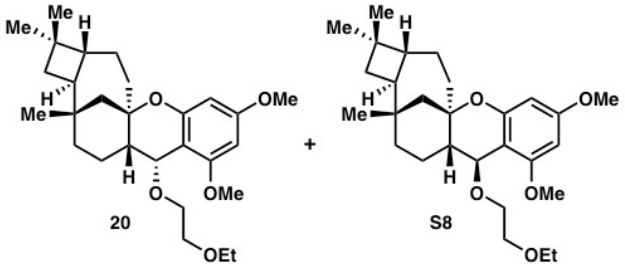
CARBON01

LMC-04-205-flash-c13

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ lchapman/ vnmrsys/ data/ LMC-04-205-flash-c13/ CARBON01.fid/fid
Title	CARBON01
Comment	LMC-04-205-flash-c13
Origin	Varian
Spectrometer	inova
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	autox7991
Number of Scans	1000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.0420
Acquisition Date	2016-06-11T18:49:53
Nucleus	13C

161.16 160.97 159.99 159.71 155.90 154.77 106.58 105.85 94.22 93.85 91.73 91.21 81.72 80.48 73.41 72.13 71.36 70.52 70.50 67.82 66.69 66.66 55.39 55.37 55.34 49.34 48.20 47.58 47.25 46.12 44.44 39.45 39.30 37.82 37.19 36.29 35.65 35.10 34.84 34.80 33.47 33.19 32.46 30.77 28.38 26.79 26.38 23.67 23.15 22.28 20.89 20.79 15.45 14.27

mixture as used in phenylation



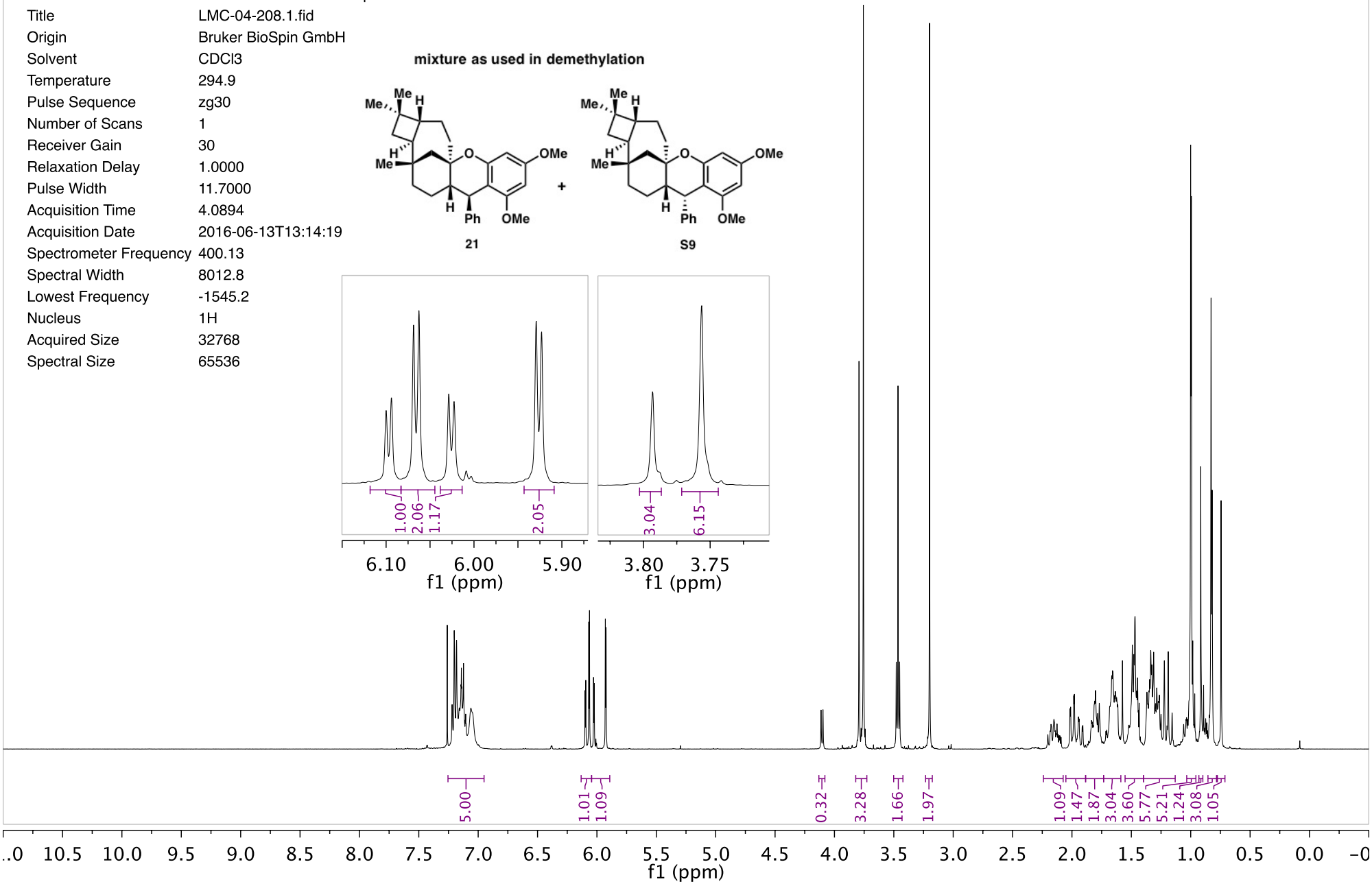
f1 (ppm)

LMC-04-208.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-208/ 1/ fid
Title	LMC-04-208.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-13T13:14:19
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

mixture as used in demethylation

21 S9

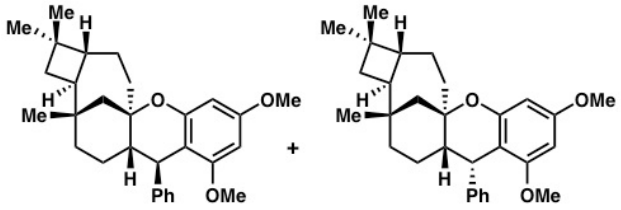


LMC-04-208.2.fid

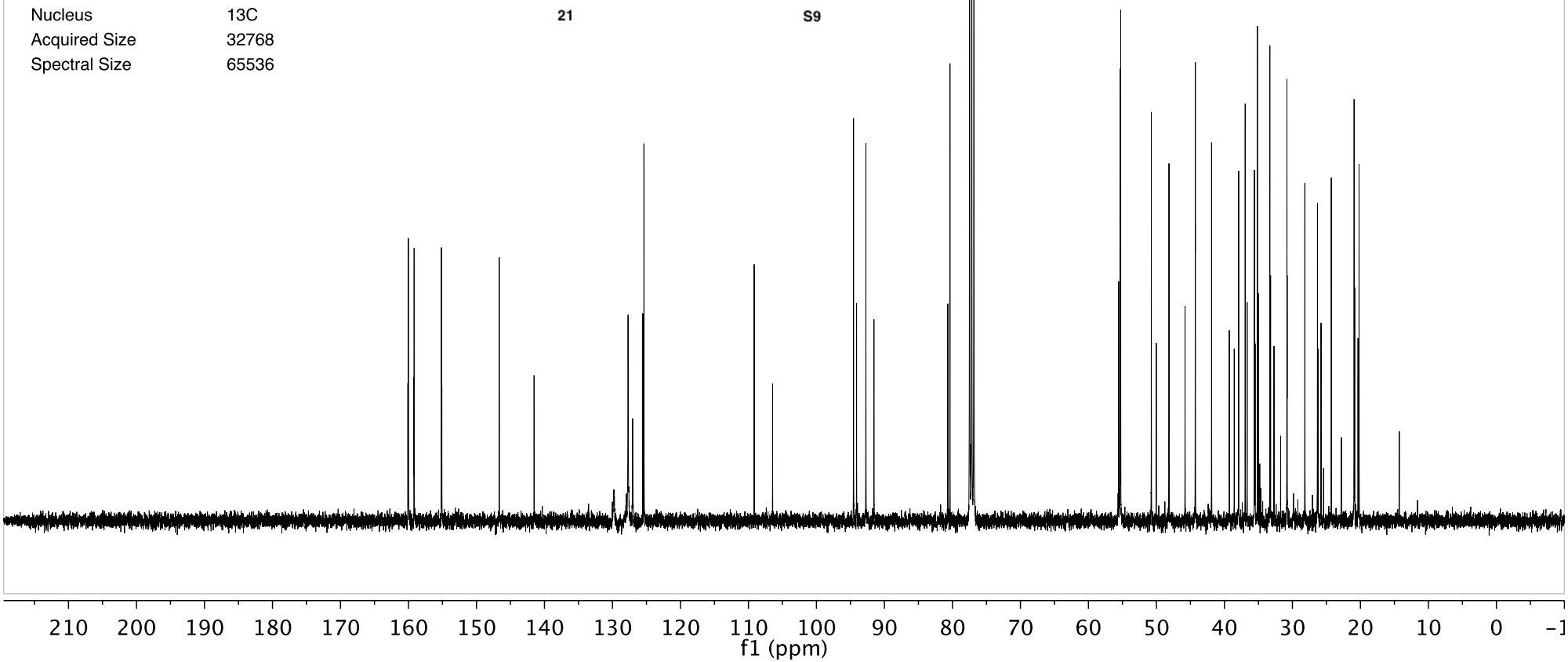
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-208/ 2/ fid
Title	LMC-04-208.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	128
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-13T13:28:03
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1947.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

160.09 160.02 159.20 159.17 155.15 155.09 146.65 141.53 129.78 128.87 127.70 127.03 125.54 125.37 109.16 106.45 94.55 94.10 92.73 91.54 80.68 80.36 55.56 55.37 55.30 55.25 50.75 50.02 48.15 45.79 44.29 44.27 41.89 39.28 37.91 36.95 36.66 35.58 35.48 35.15 35.01 33.32 33.21 32.70 30.81 30.77 28.17 26.32 25.79 24.28 20.93 20.84 20.35

mixture as used in demethylation

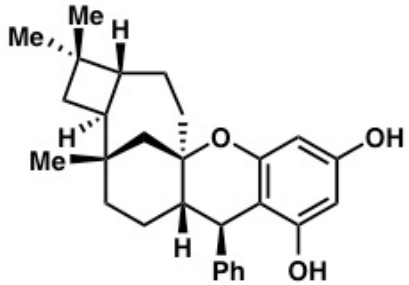


21 S9

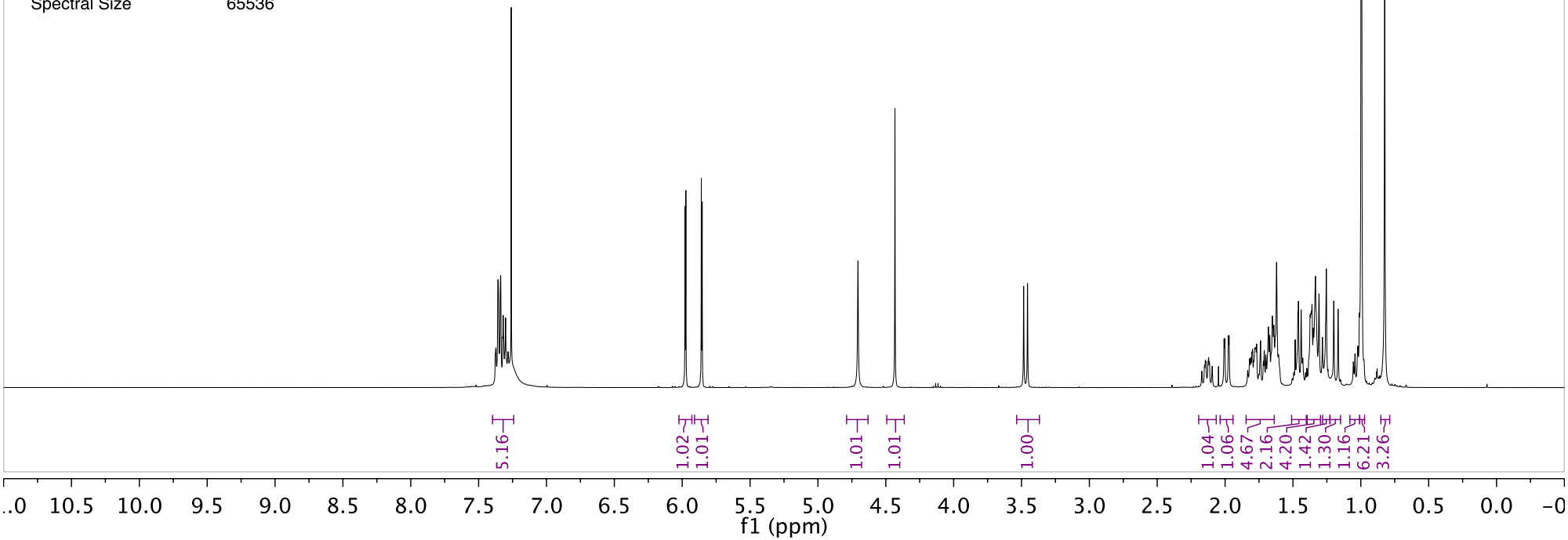


LMC-04-213-P1.2.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-213-P1/ 2/ fid
Title	LMC-04-213-P1.2.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	113
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-06-30T20:54:19
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



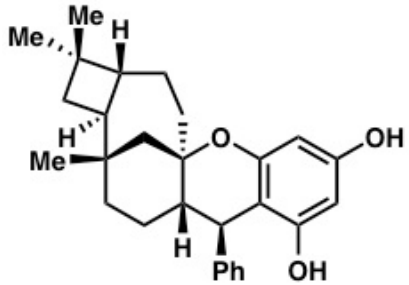
S10



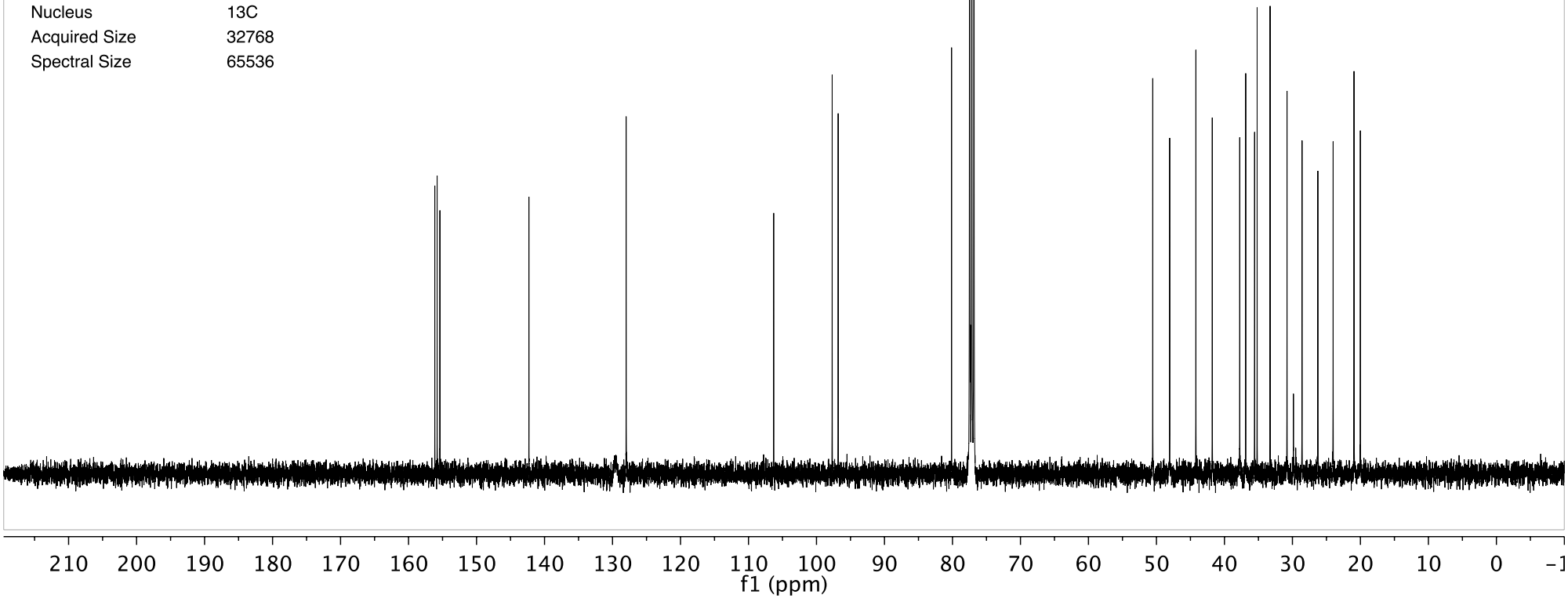
LMC-04-213-P1.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-213-P1/ 3/ fid
Title	LMC-04-213-P1.3.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	79
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-06-30T21:09:34
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

156.14
155.80
155.39
142.29
128.00
106.30
97.69
96.81
80.13
50.54
48.06
44.20
41.79
37.75
36.87
35.56
35.19
33.29
30.80
28.58
26.26
24.02
20.94
20.01



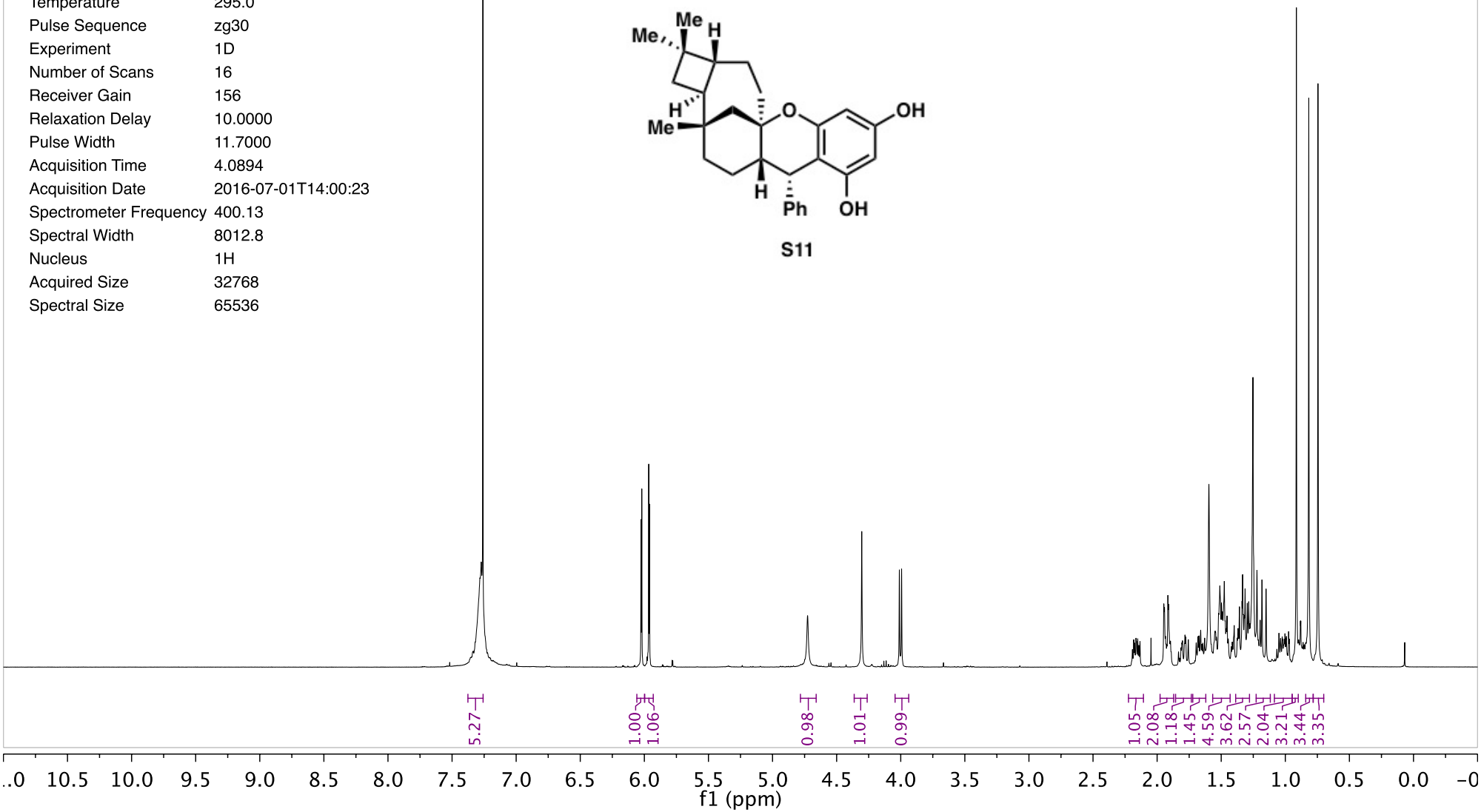
S10



LMC-04-213-P2-flash.1.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-213-P2-flash/ 1/ fid
Title	LMC-04-213-P2-flash.1.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	156
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-07-01T14:00:23
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

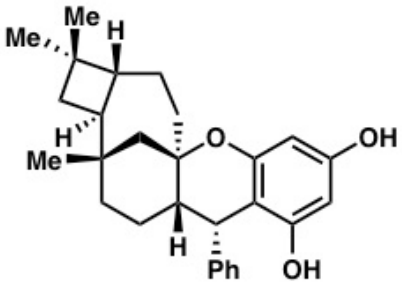
S11



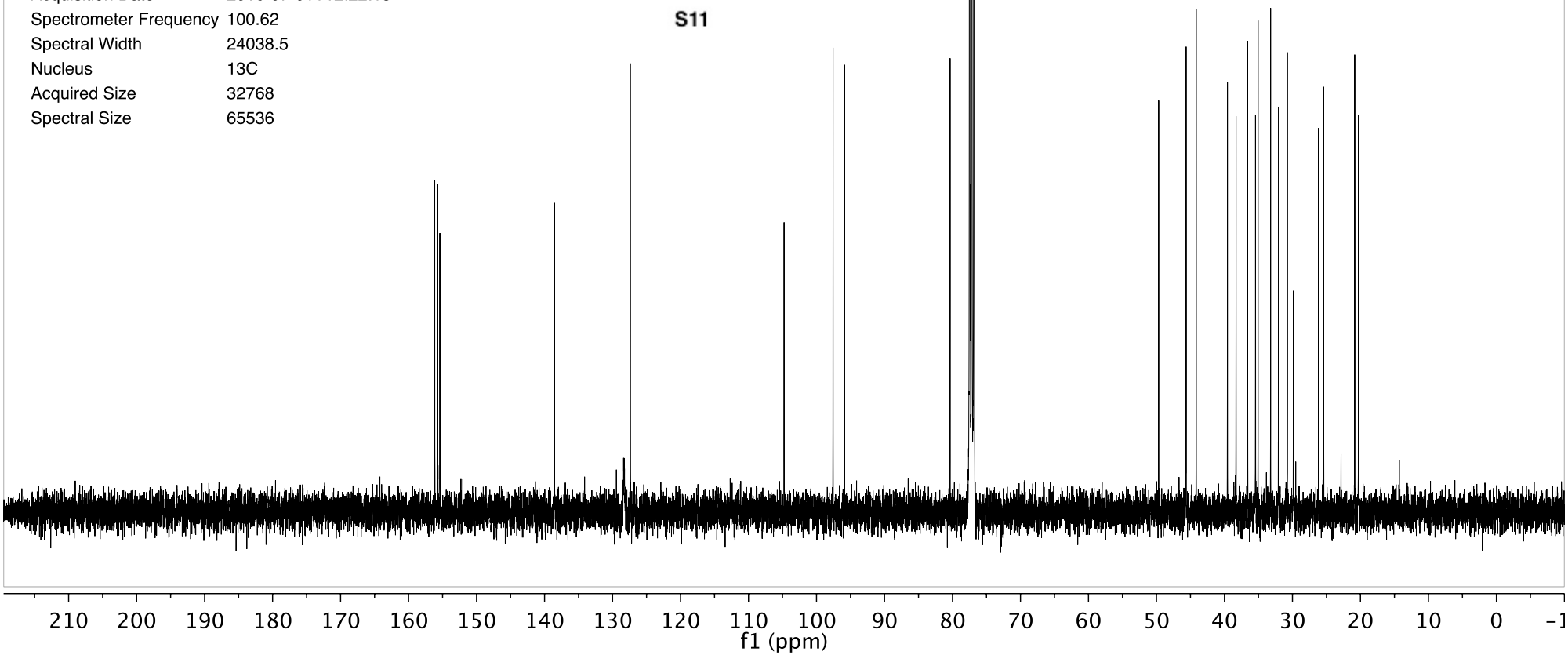
LMC-04-213-P2.2.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-213-P2/ 2/ fid
Title	LMC-04-213-P2.2.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	399
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-07-01T12:22:13
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

156.15 155.71 155.40 138.56 127.40 104.77 97.57 95.90 80.35 49.68 45.64 44.16 39.56 38.30 36.59 35.43 35.06 33.21 32.02 30.76 29.85 26.15 25.41 20.84 20.28



S11



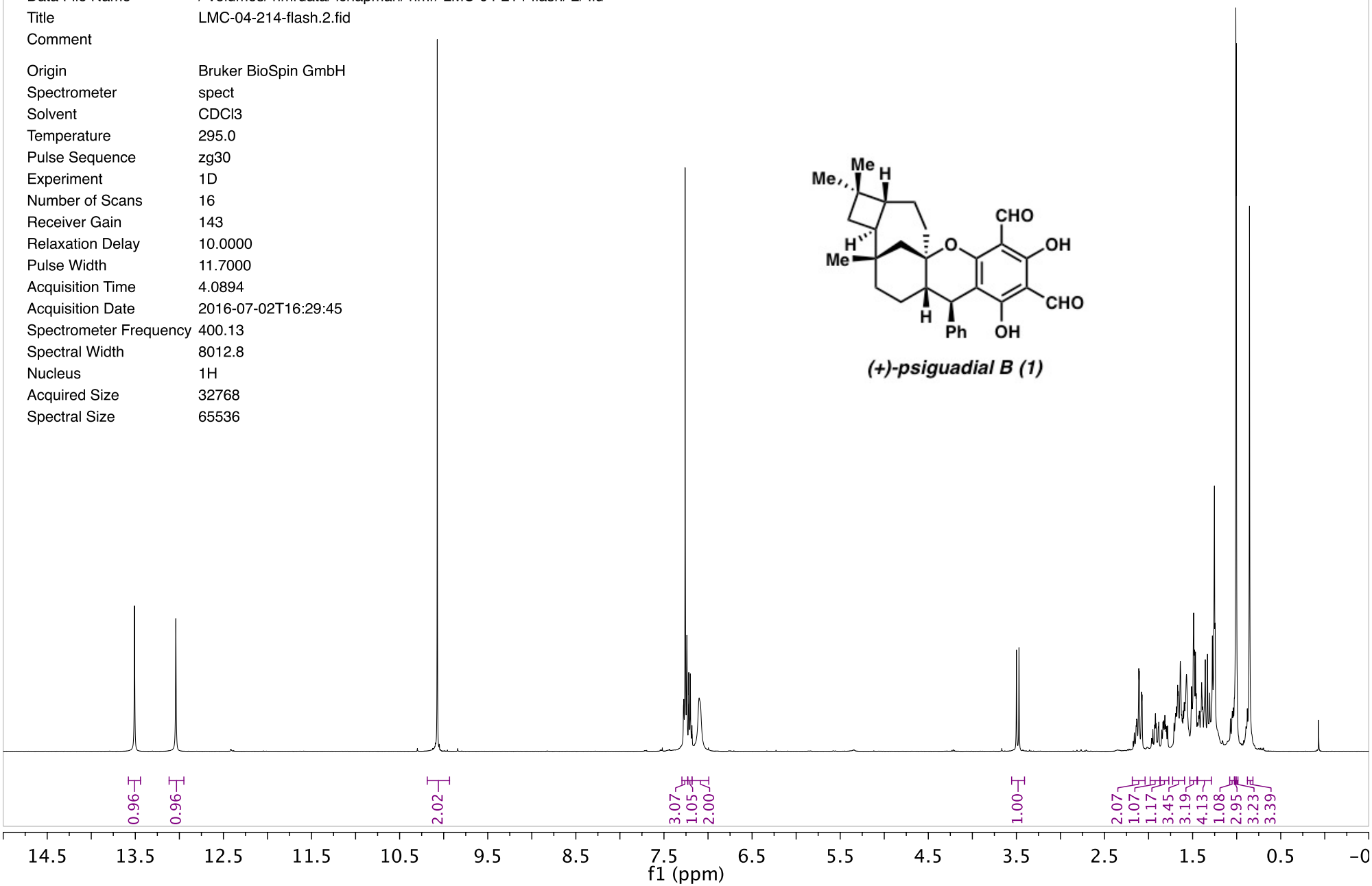
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

LMC-04-214-flash.2.fid

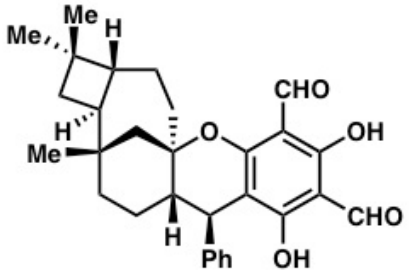
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-214-flash/ 2/ fid
Title	LMC-04-214-flash.2.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	143
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-07-02T16:29:45
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

(+)-psiguadial B (1)



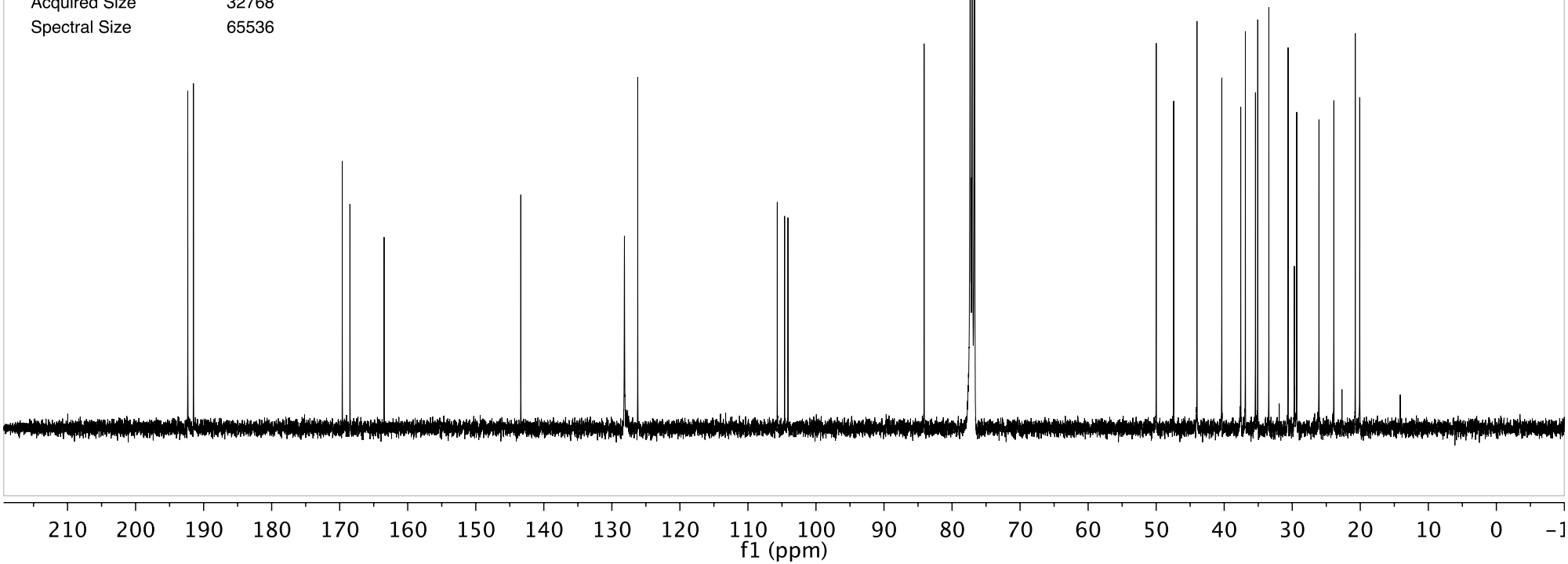
LMC-04-214-flash.3.fid

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ lchapman/ nmr/ LMC-04-214-flash/ 3/ fid
Title	LMC-04-214-flash.3.fid
Comment	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1024
Receiver Gain	72
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-07-02T17:28:52
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



(+)-psiguadial B (1)

192.35 191.50 169.62 168.50 163.47 143.38 128.15 126.20 105.69 104.61 104.12 84.10 49.99 47.42 44.00 40.36 37.57 36.89 35.40 35.07 33.44 30.61 29.34 26.07 23.88 20.74 20.08



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)